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THE LAKE SUPERIOR FIRE ASSAY FOR COPPER.

BY GEORGE L. HEATH.

Received April 24, 1902.

AS THIS method has been practically omitted from the latest editions of Peters' "Modern Copper Smelting," because of the superabundance of metallurgical material of wider interest, and as no full description has been published since the original paper of Mr. M. B. Patch was printed, many years ago, it may be of advantage to students, and to assayers, to place on record the details of present practice in refineries and stamp mills of the Lake Superior district.

The assay is adapted only to native copper occurring in veins, or bedded deposits, including the milled concentrates from the same, and also any oxides, carbonates or silicates of copper, if entirely free from sulphur. While Mr. A. H. Low,[1] of Denver, has been very successful in perfecting the "cyanide" and "iodide" assays of copper ores they are not as well adapted to native copper products[2] as the "electrolytic" assay or the Lake Superior crucible "fire assay."

In the lake region, choice of method is made according to the coarseness and richness of the sample to be treated and the tech-

[1] Peters' "Modern Copper Smelting," latest edition.

[2] *Eng. Min. J.* (1895), pp. 369 and 387.

nical accuracy required. The Heine Blue Test,[1] improved by the writer and others, is suited for rapid working tests of poor slags and tailings under 1.5 per cent. copper. For accurate work on material easily sampled, the battery assay[2] is employed, with special modifications when applied to refined copper.[3]

SAMPLING OF MATERIALS CONTAINING NATIVE COPPER.

The estimation of the metal may be required in:

I. Mine rock, as hoisted from prospecting shafts;
II. Mill concentrates, gravels and tailings;
III. Rich reverberatory furnace slags;
IV. Waste slag from "slag remelting" cupolas.

I. The low grade vein rock of the mines is well understood to carry the metal in particles of such uneven size, so unevenly disseminated in the lode, that any valuation of even a stope on anything short of a mill test of 100 to 500 tons, is of no practical value. An approximate test of any particular carload might be made by crushing to chestnut size, sampling down, grinding several pounds with repeated siftings, picking out and weighing separately the shots left on each sieve, and fusing 0.25 to 1 pound of the remaining fines in a crucible with appropriate fluxes.

II. According to the writer's experience, the "battery assay" of rich concentrates does not give as good results in the long run as the "fire assay," even if a large sample is dissolved in acid and an aliquot part by volume of the solution is taken for the electrolysis. Results would be better if aliquot parts were taken by weight, for the multiplication of slight errors in measuring flasks tends to make the result rather inaccurate.

Rich coarse material can not be accurately sampled for 1000 grain assay, when very dry, but should be wet sufficiently to make the particles adhere and a sample taken out of the material for a water determination, just before the one for copper. At refineries, concentrates are sampled by the furnace men, either at the shutes when filling hand-carts, or from the mixed pile on the charging floor of the furnace, the sample being preserved in tightly covered tin-lined copper cans.

At the C. and H. Stamp Mills, coarse gravels and other non-

[1] This Journal, 19, 24; Smith's method: *Eng. Min. J.* (1900), pp. 307–364.
[2] *Eng. Min. J.* (1895), pp. 369 and 387.
[3] *Trans. A. I. M. E.*, July, 1897.

homogeneous material have been effectively sampled down to a small portion for a "battery test" by the method of repeated siftings with removal of pellets, as suggested for vein rock (I). Some of the larger mills send the concentrates to smelters in steel cars having a cross-section somewhat like an inverted hyperbola while the smaller concerns ship in oil barrels or casks.

To avoid rehandling, the concentrates of each grade are often sampled in the cars or other containers, just before weighing, by means of a pointed tube with a slit on the side, something on the principle of the cheese tryer. This instrument seems to drive back the water a little and produce a sample that is a little too dry, and therefore a little too rich in the red metal. As the percentage of moisture continually varies in all mill products, it is necessary in all comparative work to calculate assays to dry weights of material.

Principle of the Fire Assay.—The ideal would be attained, if one could succeed in melting and reducing all the copper in a sample by fifteen or twenty minutes' fusion in a pot-furnace, without carrying any iron into the button, to be incorrectly weighed as pure copper. In practice it is found that we can so flux and fire native copper concentrates (over 40 per cent. copper) that the loss of copper in the slag can be kept at about 0.25 per cent. (of the mineral weighed) and shall be balanced by iron in the copper button, equivalent to 0.25 per cent of the original sample. It is also possible to tell, by the eye, the purity of the copper button, and the waste in the slag, within a limiting error of about 0.1 per cent. either way.

With low grades of mineral and slags, the correctness of the assay can not be told so closely by the appearance of button and slag, but a button entirely free from iron can be distinguished from one carrying enough to affect the assay result 0.1 per cent. or more. Accordingly, some laboratories fire low grades (5 to 30 per cent. copper) with such a fluxing and reducing mixture that no iron shall be carried into the button. The copper lost in the slag (usually 0.3 to 0.4 per cent.) is quickly estimated with sufficient accuracy by calculating roughly the weight of slag produced (according to formulas to be given), crushing a portion, estimating copper by blue test, and adding the total weight of copper found in assay slag to the weight of the button.

Check assays should always agree on rich grades within 0.2 to 0.4 per cent., and on poor grades within 0.2 per cent. From month to month, the fire assay, when properly conducted at a smelter, should check the output of the reverberatories, adding the slight loss in the waste slag from the cupolas.

A large assay button from rich material should be bright on all sides and have a small hole in the top with wavy or rough upper surface surrounding the cavity. A very smooth button and red slag indicates undue slagging off. If the large button has no hole and is dark on the bottom, except possibly a slight ring or film of brown on the outer edge, it will be too high in iron. Small buttons from low grades should be bright, and smooth, or with striations on upper surface, but no cavity.

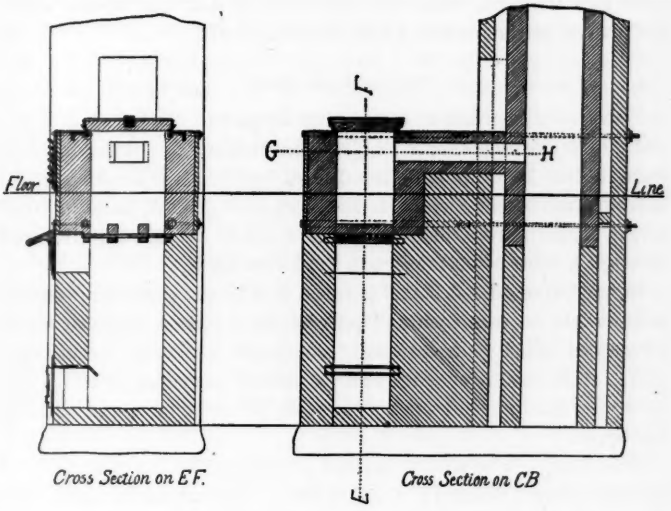
Pimples and pits, or a purple film on such a button are produced by sulphur, or by fragments of coal having dropped into the crucible. The slag from rich material (over 40 per cent. copper) should be colored black, or dark brown,—from low grades, black, or nearly so.

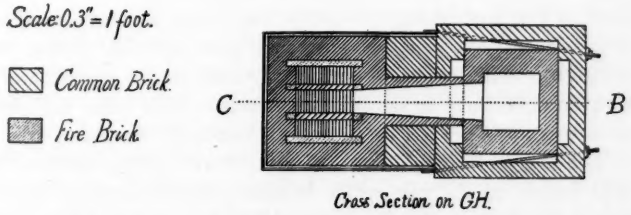
APPARATUS AND FUEL.

A pot furnace, similar to the accompanying illustration, is generally employed, but a much higher temperature and quicker heat is required than can be attained with coke and natural air-draft in twenty-minutes' time. To secure the quick, sharp heat, the furnace and stack must be brought to a high temperature before charging the crucibles, by egg-size soft coal and natural draft or by coke with an air-blast under the grate.

At the new laboratory of the C. and H. Stamp Mills, the blast produced by the smallest size Root blower is passed through a 2-inch galvanized iron pipe, to the air-tight ash-pit of the furnace. Two rows of fire-brick (2.5″ × 2.5″ cross-section) are placed across the grate, and the fuel is kept at least 2 inches above the top of these.

The mill of the Mass Mining Company is said to have installed a furnace pot heated with air-blast gasoline burners, which may be very satisfactory for a small plant. Rich grades melted in sand crucibles require a quick, sharp heat. Low-grade stuff, if fired in Denver clay crucibles, requires that the heat should be lowered to cherry-red just before charging, and that part of the soda be





placed on top of the charge in the crucible. These precautions are taken to prevent pellets sticking to the inside walls of the crucible.

Not only different classes of material, but the same grades, if fired in different makes and styles of crucibles, will require considerable changes in fluxes, especially in the reducing agent—cream of tartar. Crucibles of Denver clay, or of sand, affect the slag in a manner similar to the action of "basic," or "acid" linings in Bessemer converters. The more basic Denver crucible with round top and tightly fitting cover requires more flux and far less reducing agent, than an open-shaped triangular sand crucible. The latter is better to keep iron out of the large copper buttons

from rich material, while the Denver clay with extra thin walls has proved better for low-grade silicious stuff.

THE ACTUAL ASSAY.

Fluxes.—The cream of tartar must be 99.5 to 100 per cent. pure, and all the chemicals must be free from sulphur or sulphates. For soda, it has been found advisable to buy the "Natrona brand" sodium bicarbonate, which is fused in a large iron ladle, poured into a smooth iron dish, or ladle, to cool, and then pulverized through a sieve of 20 meshes to the linear inch.

Refined crystallized borax is fused in a Dixon graphite crucible, poured into an iron dish and pulverized to pass a 20-mesh sieve. Powdered silica is occasionally employed for very ferruginous slags, such as blister slag, and powdered hematite (Fe_2O_3) for very silicious material, such as gravels, or carbonates and silicates of copper.

Weighing.—The moist material is dumped by the assayer on a sampling board about 15″ x 20″ in area. Operators formerly used a tray made of straight-grained wood, which has to be wet with water frequently and the superfluous moisture removed with a cloth. The best thing, in every way, that we have used is a vulcanite tray, 15″ x 19″ in size, such as is sold for photographic purposes. The long side of the tray next to the operator is cut out, and we have a sampling platform which does not absorb moisture, and does not break or wear out with months of use.

The assayer quickly mixes the sample with a large steel spatula, and covers up the pile which is then pushed outward from the center and flattened to a layer about 1 inch thick and 1 foot square, or a little more. With a steel spatula (8-inch blade), vertical slices are quickly taken at regular distances apart (generally from 9 equi-distant points), dipping to the tray each time in such a manner as to make up 1000 grains on the pan of the pulp balance. This first sample is put in a dish or can, to be dried for the estimation of water, and a second portion is immediately taken for a copper assay and placed on oiled or smooth white paper.

Mineral containing 70 to 95 per cent. copper makes so little slag of itself and needs so little flux, that there would not be enough from the gangue present, to cover the button and keep it deoxidized while cooling. On this account a large stock of old assay

slag is accumulated, preferably from low grades, ground to pass a 20-mesh sieve, assayed for copper, and a certain quantity added to each crucible charge of rich material to act as a regulator and a cover for the button. If known grades, varying within narrow limits, are regularly assayed, a large quantity of complete fluxing mixture can be made up and added by measure instead of weight. Otherwise, weigh fluxes roughly, according to formulas determined by experience, mix with the spatula, transfer to crucibles and add a cover $^1/_{16}$" to $^1/_8$" deep of cream of tartar.

Scrape away the hot coals from the surface of the rows of brick in the furnace, close each crucible when in position, with a clay cover to keep out coal, poke the hot fuel around the crucibles, and fill in fresh coal (egg size) up to 1 inch below the top of the sand crucibles, or a little higher for Denver clay crucibles. The covers can be made in wooden molds from a mixture of fire-clay and ground fire-brick. Old crucible bottoms luted with clay could be employed. When using soft coal, the writer has the fire poked gently in from five to seven minutes from the start (according to the sharpness of the heat) coaled lightly in four minutes more, poked again five minutes later, and the assays taken out two to three minutes afterwards, the furnace having come to a very high heat —total time sixteen to eighteen minutes. Leave any charge not melted, until it just comes to quiet fusion. The melts should not be jarred while cooling. The success of the assay depends largely on the quick and sure regulation of the time and degree of heat.

The above manipulation is for soft coal and a double-walled tight furnace. Coke, or gasoline fuel, would require different manipulation to get the same results in the time allowed (in general not over twenty minutes for complete fusion). If low grades are to be fired in Denver "E" crucibles, the furnace and stack should be thoroughly heated, but the grate cooled down to a bright red by taking the furnace cover off for a few minutes just before firing the assays. The heat can be brought up within the time allowed, but the slower start helps to prevent pellets from sticking to the crucible.

Specimen charges are here given to show the average weights which each flux loses in melting down, and thus to indicate a method by which any one can approximately calculate what total slag will be produced in any case, and, in conjunction with the

colorimetric assay of that slag, the total copper slagged away from the button.

SMALL No. 5 HESSIAN TRIANGULAR CRUCIBLES.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Rich mill concentrates, sample = 1000 grains.	$(Cu + H_2O) = 88$	120
70 to 50 grains sodium carbonate	40	42
70 to 50 grains borax glass	0	70
250 grains assay slag (0.3 per cent. copper)	0	250
300 grains cream of tartar	75	75
Total slag		557

Actual weight of slag found to be 550 to 570 + grains.

SMALL No. 5 HESSIAN TRIANGULAR CRUCIBLES.

Composition of charge.	Losses in melting deducted. Per cent.	Calculated slag produced. Grains.
Poor (slime) mineral, 1000 grains	$(Cu + H_2O) = 33$	670
150 to 200 grains sodium carbonate	40	90
150 to 200 grains borax glass	0	150
350 grains cream of tartar	75	88
Total slag		998

Actual weight varies from 1000 to 1025 grains.

As the only appreciable impurity of copper assay buttons is metallic iron, if we desire an exact assay on any unknown sample, we have only to determine the iron in the button and the trace of copper lost in the slag, calculate both results to the 1000 grains of mineral tested, and apply the corrections to the weight of the button. This calculation will furnish also a guide as to the effects of experimental variation of fluxes and conditions of heat.

Specimen charges employed in practice at lake refineries are presented in the following table. They are based on the original paper of Mr. M. B. Patch and on the later experience of the writer and assistants with a variety of material.

It will be advisable to use the higher limiting quantity of soda on rich concentrates, when the old assay slag employed has been preserved from 1000 grain assays of low-grade material only, as such slag is proportionately lower in soda and oxide of iron than the usual slag produced years ago. Conglomerate mineral contains much more ferric and titanic oxides than the amygdaloid. In all cases there is some fine metallic iron in mill products, due to the wearing of the stamps.

Composition of Fluxes.

Class of material.	Source.	Usual limits of Cu.	Limiting per cent. of water.	Make of crucible.	Weight of sample. Grains.	Fluxes—all weights in grains. Cream of tartar.	Fused soda (Na_2CO_3).	Borax glass.	Old assay slag.	Iron ore (Fe_2O_3).	Sand (SiO_2).	Time in minutes.
[1]Mill products, rich concentrates.	Conglomerate.	90–70	1–5	H or B	1000	300	50–150	50	250			15–17
[2]As above only much coarser.	Amygdaloid.	95–75	0.5–3	H or B	1000	300	150	50–40	250			16–18
				Denver "G"	2000	300	250	100	350–375			17
Medium grades.	Conglom. or amygdaloid.	70–40	5–10	H or B	1000	300	100–150	100–150			0–100	
[3]Lean grades, table stuff, etc.	Conglomerate.	30–10	10–20	B or H	1000	300–350	150–250	200		0–50		16–18
				B or H	500	300	150–200	150–200				17
				D	1000	200	150 on top of charge. 200 mixed in.	300		0–50		16–17
[3]Lean grades, table stuff, etc.	Amygdaloid.	30–10	10–20	B or H	1000	300	200–250	200		50		16–20
				D	1000	200	150 on top. 225 mixed in.	375		0–50		16–18
[4]Reverberatory slags.	From mill concentrates.	25–10	0	B or H	500	300	200	200				18–20
				B or H	1000	400–450	320	320				20
				D	1000	350	400	400				16–20
[4]Reverberatory slags.	From melting rock, barrel work.	25–10	0	B or H	500	350	200	200		100		16–20
				B or H	1000	450	350	350		200		18–20
				D	1000	360	400	400		200		16–20
Blister furnace slag.				B or H	1000	300–400	300	300			150	17–20
Lean gravels and silicious ore.		5–10		D	1000	350+	400	400		50–100		17–20
Copper and iron oxides.	Surface ores, no sulphur.			H or B	1000	350–400	300	350			50–150	17–20

[1] Quick heat. Increase cream of tartar for black oxidized stuff.
[2] Best assay for very coarse Cu.
[3] Low grades average more silicious than years ago.
[4] Ground to pass 20-mesh sieve. Coarse shot picked out and weighed separately.

B = U Battersea Δ-shaped top.
H = Small 5 Hessian Δ-shaped top.
D = "E" special thin wall, Denver clay, O shape.

It is evident, from the foregoing description, that the Lake Superior fire assay bears no relation to the empirical matting assay in use at Swansea, but is a practical method, easily controlled when once thoroughly learned, and sufficiently accurate for all technical purposes.

NOTES ON THE ESTIMATION OF COPPER BY POTASSIUM PERMANGANATE.

By H. A. Guess.

Received April 25, 1902.

Although at various times, during the past few years, different chemists have proposed the use of an alkaline thiocyanate as a precipitant in the estimation of copper,[1] and although the results have been shown to be sufficiently accurate for technical purposes, the fact remains, that the method has made little headway, in competition with the electrolytic, cyanide, or iodide methods, in technical work, particularly in the metallurgical laboratories of the West, where the iodide method is greatly in favor.

In the iodide method, as generally practiced, the copper is first precipitated by aluminum strips, and while this precipitation is fairly rapid and complete in concentrated solutions, it is not at all so in dilute solutions of 20 milligrams or less of copper in a bulk of 150 cc. of dilute sulphuric acid. Furthermore, other metals, particularly arsenic, interfere by being precipitated along with the copper, and have to be rendered inert by oxidation with potassium chlorate. On the other hand the precipitation of copper as thiocyanate is practically complete at the moment of adding the precipitant; no other metals interfere, silver being the only other metal precipitated by an alkaline thiocyanate from an acid solution, and its thiocyanate is unacted upon by the subsequent caustic alkali treatment.

It has seemed to the writer that the main drawback to the method as so far proposed is the use of asbestos as the filtering medium, and the consequent necessity of filtering-pumps, which in a laboratory doing 100 or more copper assays in a day would render the process awkward and cumbersome. For the past six

[1] This Journal, **20**, 610; **22**, 685, *et seq*; *Am. J. Sci.*, **163**, 20-26; *Chem. Centrbl.*, **1**, (19), 1085 (1899).

months the writer has used a modified form of this process, for the estimation of copper in ores, tailings, and concentrates, doing away with asbestos as filtering material, and using filtering paper well extracted (with hydrochloric acid and hydrofluoric acid) instead, the process being briefly as follows:

From 1 to 5 grams, depending on the material for assay, are digested in an 8-ounce flask with nitric and hydrochloric acids, together with a few drops of sulphuric acid, to get rid of any lead present, the excess of acid is boiled away, the acid solution diluted, filtered, and the residue well washed on the filter. The acid filtrate is neutralized with ammonia, and then rendered just acid by a few drops of dilute hydrochloric acid; the acid cupric solution is reduced by an excess of sodium sulphite, or sulphurous acid previously nearly neutralized by sodium carbonate, and the copper precipitated as white granular cuprous thiocyanate by a slight excess of potassium or ammonium thiocyanate. The mixture is heated to boiling, the precipitate settling rapidly; the clear supernatant liquid is decanted through an 11-cm. filter, and the residue, after washing by decantation, is finally washed upon the filter, and thoroughly washed with hot water. The funnel, with its filter and precipitate, is now placed in the original precipitation flask, and a boiling 10 per cent. solution of caustic soda poured through. The operation is repeated with a further amount of the caustic solution, the filter being filled full each time to insure complete contact with all of the precipitate. Complete decomposition of the cuprous thiocyanate takes place, the equation being $CuCNS + NaOH = CuOH + NaCNS$; the insoluble yellow cuprous hydroxide remains on the filter, the alkaline thiocyanate passing through. The filter and contents are well washed with hot water, the alkaline filtrate made decidedly acid with dilute sulphuric acid, and the liberated thiocyanic acid titrated with standardized potassium permanganate at the warm temperature given to it by the hot water washings.

This method, like most other technical ones, is not perfect. The chief imperfection lies in the slight solubility of cuprous thiocyanate in the solutions present. Careful experiments as to this solubility have been made by testing the filtrate and washings from the precipitation, as thiocyanate, of weighed amounts of pure copper; the copper in solution in the filtrate is determined colori-

metrically by potassium ferrocyanide, and also by formaldoxime[1] (prepared by mixing 20 per cent. formaldehyde solution with an equimolecular proportion of hydroxylamine hydrochloride), the reaction being an intense violet coloration for the faintest traces of copper. It was found in this way that the most complete precipitation of the copper was obtained when made under the conditions above outlined, and even under these conditions the precipitate is to a slight extent soluble, the degree of solubility being most accurately determined by standardizing potassium permanganate solution with pure copper as above described, and comparing the value thus obtained with the copper value calculated from the carefully determined iron value of the same solution. Thus, comparing the equation

$$10HCNS + 12KMnO_4 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O$$

for thiocyanic acid and permanganate with the iron equation for permanganate, the copper-iron ratio is 10Cu:60Fe and the factor for copper from the iron value is 0.1892. The copper value, as determined by the precipitation (as thiocyanate) and titration, represents a factor of approximately 0.192 of the iron value, the difference between the two being due to the slight solubility of the cuprous thiocyanate and the consequent incomplete precipitation.

By standardizing the permanganate solution always against pure copper, under the same conditions as the regular assays, this error of solubility is for all technical purposes eliminated. The other imperfection of the method is the action of the filter-paper on the hot caustic alkali solution, which is very slight, and is constant for the same type of filter. It can be ascertained by running a blank filter under similar treatment, titrating, and making the correction. On an 11-cm. filter, it amounts usually to 0.3 cc. potassium permanganate, of a strength of 1 cc. equal to 2 milligrams copper.

The method has been run in parallel with the iodide on the same samples in this laboratory during the past six months, in daily assays of concentration-mill products, and in 'control' assays on smelter shipments, some 3000 determinations having been made by the method in that time. The method was begun in

[1] A. Bach: *Compt. rend.*, **128**, (6), 363-365.

a tentative way at first for tailings assays, for which neither the cyanide nor iodide methods were suitable, nor, from the arsenic and manganese present, was the usual colorimetric method. It was later adopted for the assays on crude ore and concentrates, and its results have been uniformly satisfactory. In practice it takes about the same time as the iodide method, and while, for copper to the amount of 3 per cent. and upwards, it may not offer many advantages over the latter method, which cannot well be improved upon, it is more accurate than, and distinctly superior to, either the iodide or cyanide method for small or fractional percentages of copper.

LABORATORY OF THE SILVER LAKE MINES,
SILVERTON, COLO., April 19, 1902.

[CONTRIBUTION FROM THE LABORATORY OF THE BUREAU OF INTERNAL REVENUE, U. S. TREASURY DEPARTMENT.]

THE INFLUENCE OF THE GROWTH OF MOLD UPON THE CHEMICAL COMPOSITION OF OLEOMARGARINE AND BUTTER.

BY CHARLES A. CRAMPTON.

Received April 12, 1902.

HAVING occasion to pass through the ordinary course of analysis a number of samples of oleomargarine, which had been kept in glass-stoppered bottles for about two years, I was much surprised at the results obtained. The samples, about fifty in number, had a well-authenticated history of having been taken from different packages of the same shipment of oleomargarine, a shipment which was represented by a single sample taken at the time and examined in this laboratory, giving a normal Reichert-Meissl figure.

Instead of obtaining the usual figures from the fifty old samples, as would be expected, and a close agreement among themselves, the results varied greatly; and what was still more striking, the figures given by one determination—that of the refractive index—were so low in some cases that the samples would have been classed as butter, if judged by this test alone, while others gave results normal for oleomargarine. Many of the samples were permeated with a growth of dark green mold, and on tabulating the results, it was soon seen that this was the cause of the differences, the

greatest divergence being between the samples showing a strong growth of the parasitic plant, and those showing a little or none.

The samples were divided roughly into three classes, according to the apparent amount of mold present.

Unfortunately, the amount of material was very small in any of the samples, so the only determinations that could be carried out upon all were of the Reichert-Meissl figure and refractive index, but specific gravity, Valenta, and iodine values were obtained from a few samples in each class.

The average figures for each group are tabulated together, as follows:

Group.	Reichert-Meissl value.	Refractive index at 25° C.	Specific gravity at $\frac{40°}{40°}$.	Valenta value.	Melting-point.	Iodine value.	
1. (19 samples)	4.77	1.4646	0.9084	77.00	45°	44.28	No mold.
2. (20 samples)	3.82	1.4633	0.9080	36.5	45°	43.66	Slightly molded.
3. (9 samples)	2.98	1.4610	0.8979	31.0	45°	49.81	Heavily molded.

It will be seen that the molded fat gives a much lower average figure in all the constants than the fat free from fungus, with the single exception of the iodine value. The melting-point is the same in all. The original sample which represented the same material, and which had been kept in this laboratory since December, 1899, was looked up and found to be apparently free from mold. It is not strictly comparable with the series of samples which were taken and preserved by parties other than internal revenue officers, but may fairly be presumed to approximate pretty closely the same material. Unfortunately but one determination, that of the Reichert-Meissl value, was made upon this sample at the time of its receipt in 1899. It gave R. M. = 2.42. An ample supply of material was still available which had no outward appearance of change, except that it had developed the tallowy smell incident to oleomargarine on long keeping.

Following are the results obtained:

SERIAL NO. 5264.

Specific gravity at $\frac{40°}{40°}$	0.9105
Refractive index at 25° C	1.4647
Reichert-Meissl value	4.86
Acid value (cc. normal alkali required for 100 grams fat)	17.10
Hehner value	92.70
Valenta value	68.0
Crismer value	66.3
Iodine value	47.52
Soluble fatty acids, per cent	1.04

These results correspond pretty closely with those obtained on the samples which showed no mold. Taken together, they indicate a very decided change in the values of the fat on long keeping, much more than has usually been recorded for butter-fat. The only determination made on the original, the Reichert-Meissl value, gives a considerable increase, and the other values have doubtless also changed, as some of them are quite abnormal for oleomargarine.

The figures obtained from the molded samples show a very wide divergence from the values given by those which have, presumably, been affected only by the action of the atmosphere. The Reichert-Meissl figure is much less, approaching the value ordinarily obtained from fresh oleomargarine, while the refractive index and Valenta value are about normal for butter. The specific gravity is very low, even lower than the normal figure for oleomargarine, and far below the specific gravity of the rancid samples. The iodine value shows a remarkable variation, which may be partly due to some difference in the original composition of the samples. Some of the latter gave a reaction for cottonseed oil, while others did not. The mold occurred in black spots on the fat, which penetrated entirely through the mass. The fat, on filtration, was of a reddish brown color, quite different from the color of the fat from the samples free from mold. In other respects (odor, taste, etc.) they did not differ greatly.

The samples, or rather *residues* of samples, had been kept in glass-stoppered wide-mouthed bottles. Several of the bottles were sent to Dr. Erwin F. Smith, of the Bureau of Plant Industry of the U. S. Department of Agriculture, who had kindly agreed to determine the character of the mold. He reported as follows upon the result of the examination: "All of the oleomargarine bottles furnished by you containing fungi have now been examined. The

bulk of the black substance in each one is *Coniothecium,* probably an undescribed species. The species of this form-genus are not well differentiated, and are generally named after the substratum on which they are found. So far as I know there is no record of any such fungus on butter. *Aspergillus* occurs sparingly in three of the bottles, 5058, 5060 and 5061, but not in the fourth, 5014, and I cannot bring myself to believe that it occurs in sufficient quantity to have had any influence on the oleo."

Efforts to engraft this mold upon butter have, thus far, proved unsuccessful.

On making a search of the journals for recorded observations on the effect produced by mold on the composition of fats, I found the work of Hanus and Stocky: "Ueber die chemische Einwirkung der Schimmel-pilsen auf die Butter" (*Zeitschrift Unt. Nahr. und Genussmittel,* (1900), **3**, 606).

They found that a sample of butter which had become covered with mold gave, on analysis, figures differing considerably from those originally obtained, more especially in acidity and volatile acids. They then made pure cultures of nine different species of mold and engrafted them upon butter of known composition. After three months had elapsed, they found very little change, which they explain upon the theory that the molds attack primarily the milk-sugar and protein substances in the butter, and first exert their effect upon the fat after these have been consumed. Finding that the species *Mucor mucedo* was best adapted to their purposes, on account of its mycelium penetrating deeper into the butter than the other varieties, they engrafted a culture upon butter of known composition, and allowed it to develop for a year, carrying along with it a blank sample of the same butter free from mold.

I have collected their results upon the three different samples into the following table:

Chemical constants.	Original butter-fat.	Blank control sample.	Molded sample.
Acid figure (cc. normal alkali required for 100 grams fat)	5.10	107.0	109.5
Reichert-Meissl figure	27.17	24.3	24.0
Saponification figure	226.00	222.1	217.3
Iodine figure	36.20	34.1	35.2
Volatile acids, per cent	5.10	4.96	4.90
Molecular weight of volatile acids	93.70	102.1	102.2
Free volatile acids, per cent	....	0.40	0.55
Molecular weight of free volatile acids	....	154.0	144.0
Ether figure	....	162.2	156.3

From these results they reach the conclusion that the growth of molds has a decided effect upon the composition of butter-fat, splitting up the glycerides into fatty acids and glycerol, the latter serving as a nutrient to the molds; secondarily, the free fatty acids of lower molecular weight are either oxidized to higher acids, or are reduced, the presence of aldehyde-like bodies favoring the latter hypothesis.

The original butter used in the experiment was not sterilized, and the authors noted a considerable development of *oidium,* a different type of fungus growth, in the control sample, and also in the sample engrafted with *mucor,* both species growing together. They are, therefore, unable to say just how much of the change in composition is due to the growth of *mucor,* how much to *oidium,* and how much to the action of air and light solely.

Laxa[1] found that the molds, *Oidium, Penicillium,* and *Mucor,* effect a hydrolysis of butter-fat, as do also the yeasts, though to a less extent. I have no access to the original paper.

The most recent and conclusive work upon the fat-destroying power of molds is that by Koenig, Spiechermann and Bremer,[2] whose paper contains also a comprehensive review of the results recorded by other observers in this direction. They investigated the changes produced in the composition of cottonseed meal, along with other food and fodder materials, by various classes of micro-organisms. They found a well-marked effect exerted upon the oil by both bacterial and fungous growths, under conditions favoring their development. I will quote here the more pertinent of their conclusions:

"8. Experiments with pure cultures of *mycelium* fungi obtained from cottonseed meal, and with other species grown upon sterilized cottonseed meal, and also upon artificially prepared nutrient material containing fat, have shown that the *mycelium* fungi are abundantly able to use as a source of carbohydrate both fats and the higher fatty acids (liquid and solid).

"9. Hand in hand with fat consumption goes always the splitting up of the fat, yet this reaction never extends to the entire body of fat present, and it varies in strength with different micro-organisms.

* * * * * * *

[1] *Arch. Hyg.,* **41,** 119; *J. Soc. Chem. Ind.,* **21,** 268 (1902).
[2] *Zeitschrift Unt. Nahr. und Genussmittel* **4,** 721 and 769 (1901).

"11. The fat is apparently, for the greater part, decomposed directly into carbonic acid and water."

The investigation showed that bacteria resisting a sterilization temperature of 100° (so-called *kochfester* bacteria) were capable of bringing about the decomposition of fat, though not to the same extent as the fungous growths which are visible to the eye.

The results obtained by me strengthen the conclusions reached in the investigations outlined above, and have two important bearings:

First, a most practical bearing upon the interpretation of analytical results; and second, upon various unsolved problems of the constitution and metamorphosis of the glycerides. In regard to the first, the obvious lesson is that no reliance can be placed upon the ordinary constants used for the detection of foreign fats in butter when the sample in question has been invaded by the growth of mold. An *apropos* instance may perhaps be cited in a communication by H. Droop Richmond in the *British Food Journal,* (1903) **3**, 393. The writer discusses the anomalous results obtained in the analysis of Russian butter in certain important legal cases before the English courts. He is unable to account for the figures obtained, some of which point strongly towards adulteration; but he mentions, incidentally, the fact that his samples showed the growth of a mycelium fungus, and this probably affords the key to a solution of the entire matter.

A sample of butter, recently brought to this laboratory, showed a growth of mold upon a portion of its surface. A separation of the molded and unmolded portions was made, and the following values obtained. The identity of the mold was not established.

SERIAL NO. 5109.

	Without mold.	With mold.
Reichert-Meissl value	26.79	25.53
Refractive index at 25° C	1.4596	1.4594

These results confirm the observations of Hanus and Stocky to the effect that the growth of mold in butter produces a slight but distinct decrease in the Reichert-Meissl value.

From another sample, however, I obtained values which showed a much more radical change in composition, and which are, so far as I am aware, the lowest in some respects ever reported from a genuine butter. This sample, Serial No. 5385, was received in

February, 1899, at which time it gave a Reichert-Meissl value of 29.92. For some reason it had not been thrown out, and when examined in March, 1902, after remaining three years undisturbed in a tin can, it was found to be thoroughly permeated with a reddish brown mold.

This was examined by Dr. Smith, who reports it as *Coniosporium sp.?* He found also *Penicillium sp.?* in small quantity.

A fair quantity of the filtered fat was obtained, which was of a rather deep shade of orange-yellow. It gave the following values:

SERIAL No. 5385.

Specific gravity at $\frac{40°}{40°}$	0.8978
Refractive index at 25° C	1.4578
Reichert-Meissl value	13.09
Acid value (cc. normal alkali required for 100 grams fat)	141.75
Iodine value	40.66

The Reichert-Meissl value is less than half of the original; the refractive index is abnormal, being lower than that obtained from butter; and the specific gravity is rather lower than the usual "oleo" figure.

Returning to the results obtained from the oleomargarine which had been kept a long time, but which showed no apparent growth of mold, Serial No. 5264, the values approach figures normal for butter, as is also the case with those samples in the series which showed little mold. In further confirmation of this, three other samples of oleomargarine were selected, none of which showed visible evidence of the presence of mold. These samples were received during the months of February and March, 1899, and had consequently been kept (in tin cans) over three years. The following table gives the Reichert-Meissl values at the time of their receipt, and at the time of their re-examination; also the refractive indices, specific gravity, and acid values.

		1902.			
Serial No.	1899. Reichert-Meissl value.	Reichert-Meissl value.	Refractive index.	Specific gravity at $\frac{40°}{40°}$.	Acid value (cc. normal alkali required for 100 grams fat).
5386	3.30	4.26	1.4639	0.9102	43.8
5387	1.76	5.60	1.4656	0.9159	5.0
5388	2.20	5.26	1.4679	0.9144	6.1

The changes brought about in the Reichert-Meissl values are fully as radical as in the other samples; the specific gravities also, while no comparison can be made owing to lack of data on the samples as originally received, have manifestly increased, as they are as high as butter normals.

From an analytical standpoint, these changes in composition are even more dangerous than those produced by the growth of a micro-organism like mold which is visible to the eye. That they are due entirely to the ordinary action of air and light cannot be believed, and this leads up to the consideration of the theoretical bearing of the results, particularly upon the nature of rancidity changes. Most of the authorities on fats and oils (Lewkowitsch, Wright, etc.) accept as conclusive the results of Ritzert[1] who found that pure lard was not turned rancid by bacteria introduced into it, as they soon died; and that fat sterilized at 140° became rancid on subsequent exposure to light and air.

I am not now in a position to oppose specifically the conclusion that a fat cannot become rancid without the presence of micro-organisms, although I hope to be able soon to repeat the experiments of Ritzert upon this point. But I do not think there can be any room for doubt that the growth of micro-organisms plays a highly important rôle in the changes which occur in fats and oils under ordinary conditions of exposure. Even if it be granted that the breaking up of the glycerides may eventually take place merely from the presence of oxygen, it is certain that the change is greatly promoted and expedited by their development.

I think it may safely be asserted, for the edible fats, at least, where the presence of nitrogenous and other non-fatty matter affords a sprouting medium for such growth, that the greater part of the changes embraced under the general term "rancidity" is due to the action of micro-organisms, or to the enzymes resulting from their development. The most rational explanation of the results obtained on the samples of oleomargarine appears to me to be as follows: The glycerides, exposed to the cool damp air of the refrigerator, and in contact with the nitrogenous matter derived from the milk used in the process of manufacture, underwent a gradual decomposition, probably induced and promoted by bacterial growth, with the formation of the lower fatty acids. This pro-

[1] *Untersuchungen uber d. Ranzigwerden der Fette*, Inaug. Diss., Berlin, 1890.

gressed to a very considerable degree, giving the high results obtained for volatile acids and specific gravity obtained from the samples which showed no mold. The germs of the *Coniothecium* fungus having gained access to the fat, or, more probably, having been contained in it originally, and their growth being started by the favorable conditions resulting from the splitting up of the glycerides, attacked the liberated fatty acids and glycerides, and consumed them in proportion to the growth. The growth of the fungus produced further decomposition and a further consumption of fatty acids, with a preferment for those of lower molecular weight, until the remaining mixture of fat and free acids gave the diminished values for volatile acids and specific gravity obtained from the molded samples.

Experiments are now in progress in this laboratory having the object of a more exact investigation of the changes brought about in fats by the growth of mold. This I hope to accomplish by growing pure cultures upon a large quantity of fat of known composition. As these experiments will necessarily require a long time for completion, I report the results set forth above as a preliminary paper.

My thanks are due to Mr. F. E. Simon and Mr. A. B. Adams of this laboratory, by whom the principal part of the analytical work was performed.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 65.]

AN ELECTROLYTIC STUDY OF PYRORACEMIC ACID.[1]

BY GEORGE W. ROCKWELL.

Received March 12, 1902.

WISHING to study the effect both of the oxidizing and reducing power of the electric current upon an organic body, aiming at the same time to fix the conditions so that other persons upon repeating the experiments might well expect to get similar results, I selected pure pyroracemic acid for my investigation.

The apparatus employed in the experiments consisted of a beaker glass, a porous cup, which served as a septum for the separation of the anode and cathode liquids, and two platinum

[1] From author's thesis for Ph.D. degree, 1900.

electrodes of 100 sq. cm. surface each. When hydrochloric acid was used as an electrolyte, an anode of carbon was substituted for that of platinum. In several instances lead electrodes were used; these were of the same surface as that of the platinum electrodes.

The solvent generally employed was ordinary alcohol (about 95 per cent.). The concentration of the solution electrolyzed depended upon the conditions assumed for each experiment.

When a temperature sufficient to volatilize alcohol was used, a return condenser was inserted into the neck of the porous cup, by means of a large rubber stopper.

The current employed in most of the experiments was from an ordinary 110-volt incandescent light circuit, which was adjusted by means of lamps and wire resistance frames, so that a current ranging from 0.1 to 10 amperes could be used. Sometimes the current from five chloride accumulators, and in one instance only, that of eight gravity cells of the ordinary type was applied.

The temperature was taken with an ordinary thermometer. The readings were made with the thermometer inserted in the cathode liquid.

Attempts were made to estimate the various products of the electrolysis quantitatively, but I am convinced that they have fallen short in every case.

EXPERIMENTAL PART I.

The experiments considered in this part are those in which the oxidizing action of the current was studied.

A. Oxidation in Sodium Hydroxide Solution.

Experiment 1.—This was conducted with the following conditions:

Pyroracemic acid	5.56 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Temperature	Ordinary.
Time	22 hrs.
Normal density, N. $D._{100}$	1.3 amperes.
Voltage	$3^2/_3$ volts.

Water sufficient to dissolve the sodium hydroxide was also added.

A Bunsen voltameter containing alkali was inserted in the cir-

cuit, in order to compare the volumes of the electrolytic and experimental gases given off in the same period of time.

One comparison was made and the experimental gas analyzed. The results of the analysis are as follows:

Volumes of the gases disengaged in the same time:

Electrolytic	79.1 cc.
Experimental	12.4 cc.
The experimental gases were	0.4 cc. CO_2
	2.8 cc. O
	9.2 cc. N

This analysis shows the presence of air and as the experimental gases evidently did not escape fast enough to prevent the air from entering in at the joints of the apparatus during the time of their collection, no more comparisons were made.

Toward the close of the experiment it was noticed that the brilliancy of the incandescent lamps, through which the current was conducted, was greatly diminished, until finally the filaments became dull red in color. This indicated that the solution in the porous cup had become greatly deficient in its power of conductivity, but the real cause of this behavior was not noticed at the moment.

The contents of the porous cup were poured into a beaker glass, where they were discovered to have changed color, passing from a straw-yellow to a cherry-red. The solution was allowed to stand over night and then was filtered through a coarse filter-paper to remove silica, after which it was distilled over a free flame. The distillate possessed an ethereal odor.

Experiment 2.—The oxidation was made with:

Pyroracemic acid	4.33 grams.
Sodium hydroxide	5 grams.
Alcohol	50 cc.
Time	$5\frac{1}{2}$ hours.
Temperature	Ordinary.
N. D_{100}	1.3 amperes.
Voltage	$3\frac{1}{8}$ volts.

Water sufficient to dissolve the sodium hydroxide was also added. In this experiment the experimental gas was collected after the current had been allowed to act for some time. It was analyzed with the following results, 100 cc. of gas being taken as sample each time.

Analysis I.

100 cc. of gas taken during first and second hours:

	cc.
Carbon dioxide	24.6
Oxygen	9.6
Carbon monoxide	14.6
Nitrogen	51.2

Analysis II.

100 cc. of gas taken during third and fourth hours:

	cc.
Carbon dioxide	73.2

Analysis III.

100 cc. of gas taken during fourth and fifth hours:

	cc.
Carbon dioxide	59.6
Oxygen	9.4
Carbon monoxide	13.6
Nitrogen	17.4

These gas analyses show that the action of the current had taken effect, either in oxidizing some of the carbon of the pyroracemic acid to carbonic acid, or that it had caused a rupture in the molecule $CH_3CO\,COOH$, splitting off carbon dioxide.

The contents of the porous cup were treated as above, and it was noticed at this juncture, that the distillate possessed the odor of acetic ether.

Experiment 3.—About 29 grams of pyroracemic acid were used; all the other conditions were not noted, the object being to get a better insight into the gases by a more rapid evolution of the same from the experimental cell. They were collected in samples of 100 cc. after the current had acted for several hours.

Analysis I.

	cc.
Carbon dioxide	92.8
Oxygen	3.0
Carbon monoxide	1.0
Nitrogen	3.2

Analysis II.

	cc.
Carbon dioxide	85.0
Oxygen	7.8
Carbon monoxide	2.8
Nitrogen	4.4

The samples for these analyses were collected several hours apart and show conclusively that the action of the current had either caused an oxidation or a breaking-down in the molecule of the pyroracemic acid.

The electrolyte in this experiment possessed the color and odor previously observed.

Experiment 4.—Here the conditions were:

Pyroracemic acid	19.87 grams.
Sodium hydroxide	40 grams.
Alcohol	150 cc.
Water	100 cc.
Temperature	Ordinary.
Time	90 hours.
N. $D._{100}$	1.3 amperes.
Voltage	3–4 volts.

Thus far I had collected the gases escaping from the experimental cell over the same water, and I observed that the latter possessed an odor characteristic of aldehyde. The electrolyte, also, if noticed carefully, was found to bear an aldehydic odor, besides that of acetic ether and alcohol.

As a consequence of these observations, an Erlenmeyer flask containing ether was inserted into the exit tube leading to the vessel in which the water was contained, and allowed to remain for several hours, after which the flask was removed and dry ammonia gas passed through the ether. A white precipitate of aldehyde ammonia was the result.

Experiment 5.—The amounts of material varied but little from those in the preceding experiments.

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	85 cc.
Temperature	30°–80° C.
Time	8 hours.
$N.D._{100}$	2.5 amperes.
Voltage	6–20 volts.

With the anode liquid made up as above indicated, the experiment was started and allowed to continue until it became almost a non-conductor, as observed in some of the preceding experiments. The temperature and voltage increased while the amperage naturally decreased.

The gases were passed through ether, as before, and the aldehyde precipitated by ammonia. The yield in this experiment was equal to 0.9656 gram aldehyde, or 19 per cent. of the theoretical.

Here it might be the proper place to offer some theoretical explanation of the reactions so far observed.

First, it seems that aldehyde is the first product of the oxidation, and it appears to be formed by the breaking-down of the acid molecule in this manner:

$$CH_3COCOOH = CH_3CHO + CO_2.$$

Secondly, from the very characteristic odor of acetic ether, which is, without a doubt, present, I conclude that it must be formed from the acetic acid, which would naturally be the next product of the oxidation, and the alcohol present in the solution thus:

$$CH_3CHO + O = CH_3COOH,$$

$$CH_3COOH + C_2H_5OH = CH_3COOC_2H_5 + H_2O.$$

The singular fact about this is that these reactions took place in a solution that was strongly alkaline to begin with. But as we know that such ethers are generally formed in acid solutions, the pr sence of acetic ether here gives very reliable evidence of the formation of acetic acid as a second product.

Thirdly, another reaction, in all probability, takes place thus:

$$CH_3COOC_2H_5 + NaOH = CH_3COONa + C_2H_5OH.$$

By this reaction sodium acetate would be formed, regenerating the alcohol.

All these reactions, of course, are only of theoretical interest.

Experiment 6.—The material used was:

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	110 cc.
Temperature	60°–80° C.
Time	5 hours.
N. $D._{100}$	2.5 amperes.
Voltage	6–56 volts.

The cell containing this solution was placed upon a water-bath and was attached to a return condenser, which served to condense any vaporized alcohol. A low flame was applied to keep the temperature within the limits given. A long glass tube connected the

top of the condenser with two Erlenmeyer flasks, which contained anhydrous ether. This tube served to conduct the exuding gases through the ether.

The experiment was interrupted when the bubbles passed slowly through the ether and in place of the return condenser an ordinary Liebig condenser was attached to the anode chamber and the experiment continued. A liquid very like acetic ether in odor began to distil over at 76°-77° C., but almost immediately the temperature rose to 78° C., when alcohol came over. The distillate was collected for several minutes and it had all the appearance and odor of those residual liquids obtained from the ether extractions in the previous experiments.

The change in color of the anode liquid was undoubtedly due to the usual effect of an alkali on aldehyde.

The precipitated aldehyde ammonia in this case equaled 0.7980 gram, equivalent to 0.5755 gram of aldehyde, or one-tenth of the theoretical yield.

The anode liquid was evaporated on the water-bath after filtration, when it gave a tarry residue, from which nothing could be sublimed.

Experiment 7.—The same conditions were observed as given above for Experiment 6, with the exception of the time, which was cut down to four hours and twenty minutes. In this experiment the ether was chilled by ice-water and a copious precipitate of aldehyde ammonia was obtained. It was not weighed.

Experiment 8.—This was performed according to the conditions under Experiment 6. A better yield of aldehyde was obtained. The aldehyde ammonia equaled 4.88 grams, equivalent to 3.41 grams of aldehyde, or about three-fifths of the theoretical.

Experiment 9.—This experiment was performed with the following conditions:

Pyroracemic acid	10 grams.
Sodium hydroxide	10 grams.
Water	110 cc.
Alcohol	100 cc.
Time	$7\frac{1}{2}$ hours.
Temperature	50° C.
N. $D._{100}$	1.35–0.85 amperes.
Voltage	5–40 volts.

Lead electrodes were used. It is seen, from the above data re-

garding amperage and voltage, that the action proceeded along the same line as it does with the platinum electrodes. The aldehyde was precipitated as aldehyde ammonia, as before; it equaled 1.5522 grams. It was thought that the lead peroxide being formed at the anode might aid in the oxidation, but it seems to have no action.

Experiment 10.—The conditions observed here were similar to those of Experiment 9, with the exception of the temperature, which was raised to 70° C. For the platinum electrodes, two carbon electrodes of 45 sq. cm. were substituted. This experiment yielded aldehyde upon the usual treatment. It was not weighed.

It was thought that possibly the carbon would produce milder oxidation, by uniting with the oxygen to form an atmosphere of carbon dioxide, and thus retard the oxidation. In this manner it was hoped to form acetyl superoxide, and then have this break down into diacetyl, thus:

1. $\begin{matrix}CH_3COCOOH\\ \\ CH_3COCOOH\end{matrix} + OOO = H_2O + 2\overline{CO_2} + \begin{matrix}CH_3COO\\ |\\ CH_3COO\end{matrix}$

2. $\begin{matrix}CH_3COO\\ |\\ CH_3COO\end{matrix} + OO = \begin{matrix}CH_3CO\\ |\\ CH_3CO\end{matrix} + 2\overline{O_2}$

As Schall in 1871 claimed to have obtained a persulphide of an analogous formula to that given to acetyl superoxide, it seems, reasoning by analogy, that if diacetyl exists at all it should be obtained from pyroracemic acid, if any acid is to yield it, according to the above indicated reactions.

B. Oxidation in Sulphuric Acid Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	100 cc.
Temperature	60°–80° C.
Time	$4\frac{1}{2}$ hours.
N. $D._{100}$	2.5 amperes.
Voltage	3 volts.

This experiment was conducted in an apparatus similar to that employed in the sodium hydroxide solutions. Aldehyde ammonia

was precipitated in the usual manner. The anode liquid had the odor of acetic ether.

Experiment 2.—In this experiment conditions similar to those in Experiment 1 were observed. The anode liquid was shaken out with ether and distilled as usual; the resulting distillate was of the same nature as those produced by the experiments made in sodium hydroxide solution. This is a further proof of the production of acetic acid, as here we have the production of acetic ether in acid solution.

Experiment 3.—The following conditions were observed:

Pyroracemic acid	10 grams.
Alcohol	100 cc.
Sulphuric acid (conc.)	25 cc.
Temperature	50° C.
Time	27 hours.
N. $D._{100}$	0.45 ampere.
Voltage	$2^2/_3$ volts.

The thought entertained here was that with low pressure and density there was a possibility of obtaining diacetyl in sulphuric acid solution. No attempt was made to collect the gases. An inverted condenser was used to return any alcohol. The anode liquor was extracted with ether several times, but nothing new was found.

Experiment 4.—The conditions in this experiment were:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	100 cc.
Time	$7^1/_2$ hours.
Temperature	60° C.
N. $D._{100}$	1.4 amperes.
Voltage	$4^1/_3$ volts.

Lead electrodes were employed. Aldehyde was precipitated by ammonia, but was not weighed for the reasons already noted. The anode liquid yielded nothing new.

Experiment 5.—The conditions observed here are similar to those under Experiment 4, with the exception of time and density. The time was three hours and N. $D._{100} = 0.9$ ampere. Carbon electrodes were used. Aldehyde and the other products were obtained. This experiment was interrupted at the point when it

was supposed that the aldehyde would begin to come off, but such a point was not found.

C. *Oxidation in Hydrochloric Acid Solution.*

Experiment 1.—The following conditions were observed:

Pyroracemic acid	10 grams.
Hydrochloric acid (conc.)	30 cc.
Alcohol	100 cc.
Time	5 hours.
Temperature	60°–70° C.
N. $D._{100}$	2.5 amperes.
Voltage	5 volts.

A carbon plate was substituted for the platinum anode in these experiments, otherwise they were conducted as those which precede them. Upon the passage of ammonia gas into the chilled ether a white coloration was produced, but it disappeared after a short time. This was probably due to a little volatilized hydrochloric acid gas in the ether, or perhaps there was sufficient water in the ether to dissolve it. The anode liquid was treated as above, but gave nothing other than what had been noted previously.

Experiment 2.—Here I used:

Pyroracemic acid	20 grams.
Hydrochloric acid (conc.)	60 cc.
Alcohol	150 cc.
Time	24 hours.
Temperature	50° C.
N. $D._{100}$	0.4 ampere.
Voltage	18 volts.

The anode in this experiment was a common graphite pencil with the wood removed at both ends. My hope was that I might obtain diacetyl, but without avail.

Experiment 3.—Material slightly varied again:

Pyroracemic acid	20 grams.
Alcohol	100 cc.
Hydrochloric acid (conc.)	30 cc.
Temperature	40° C.
Time	10 hours.
N. $D._{100}$	1.35 amperes.
Voltage	5 volts

A carbon plate was used. The anode liquid, analyzed as before, revealed nothing new.

D. Oxidation of Certain Salts of Pyroracemic Acid.

The magnesium, sodium and iron salts were made with care and their solutions electrolyzed with the hope of obtaining diacetyl, but it was not found.

E. Oxidation in Sodium Carbonate Solution.

Experiment 1.—Here I used the following:

Pyroracemic acid	10 grams.
Time	6 hours.
Temperature	30° C.
N. $D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. The cathode liquid was also a solution of sodium carbonate.

It was found that after a time the anode liquid became acid. The escaping gases were tested for carbon dioxide and found to contain 93 per cent. This indicates action similar to that produced in a sodium hydroxide solution.

Experiment 2.—Observing that no diacetyl had as yet been obtained, it was suggested to keep the anode liquid perfectly alkaline by means of sodium carbonate added from time to time; also to keep the cathode liquid as nearly neutral as possible by running a stream of carbon dioxide into the same. With these precautions all of the following experiments were directed to the formation of diacetyl.

Pyroracemic acid	20 grams.
Time	$9\frac{1}{2}$ hours.
Temperature	30° C.
N. $D._{100}$	1.35 amperes.
Voltage	6 volts.

The pyroracemic acid was dissolved in 100 cc. of water and neutralized with sodium carbonate. A small addition of the same was made every half hour. The anode liquid was taken out and distilled over a free flame. The distillate was salted out with common salt and redistilled. This procedure gave a greenish yellow distillate, with a color very like that of diacetyl. This was dehydrated over calcium chloride and distilled again. It retained the same color, but the odor was like that of a weak solution of the pyroracemic acid itself, after being boiled.

The boiling-point of diacetyl (87°-88° C.) was never approached in the distillation of this substance.

Experiment 3.—Again I employed the following:

Pyroracemic acid	20 grams.
Water	100 cc.
Time	10 hours.
Temperature	30° C.
N. $D._{100}$	1.8 amperes.
Voltage	10 volts.

The anode liquor was acidulated with dilute sulphuric acid and then distilled; the distillate was salted out as before and redistilled. It gave a greenish yellow distillate, which was treated according to the method of Pechmann.[1] In accordance with this, normal potassium hydroxide was added to the solution to alkaline reaction, but it did not become colorless or a faint brown as Pechmann asserts. It, however, became a light yellow in color. It was then acidulated with dilute sulphuric acid and extracted several times with ether. The ether was distilled off and a yellowish green substance was left instead of a colorless oil as directed.

The object of this treatment was to form if possible the aldol of diacetyl.

From what I obtained from the ether extractions, I attempted to produce *p*-xyloquinone, by treatment with potassium hydroxide, which would constitute a conclusive test for diacetyl. This, however, was not obtained. The *p*-xyloquinone is described as a golden yellow crystalline compound, crystallizing from alcohol in needles and subliming undecomposed. No product of such characteristics appeared in the attempted transformations.

Still laboring under the impression that possibly that greenish yellow material might be the sought-for substance, several experiments were tried, some with the same conditions as those given above and others with conditions slightly different. The anode liquids were all treated as has been described, but no test for diacetyl revealed its presence.

EXPERIMENTAL PART II.

In the reduction of pyroracemic acid the porous cup was made the cathode chamber.

[1] *Ber. d. chem. Ges.*, **28**, 1846.

A. Reduction in Sodium Hydroxide Solution.

Experiment 1.—The following material was employed:

Pyroracemic acid	5 grams.
Alcohol	50 cc.
Water	50 cc.
Sodium hydroxide	8 grams.
Temperature	Ordinary.
Time	7 hours.
N. $D._{100}$	0.45 ampere.
Voltage	$3^1/_3$ volts.

The lactic acid in the cathode liquid was estimated according to the directions in Beilstein's "Handbook" as follows: It was acidulated with dilute sulphuric acid and extracted with ether several times. The ether was evaporated and the residual liquid heated in a porcelain dish for some minutes on a water-bath to expel any dissolved ether. Lead acetate was added to remove any sulphuric acid present. The lead sulphate formed was filtered off and more lead acetate added together with alcoholic ammonia (alcohol 90 per cent., ammonia 10 per cent.) until no further precipitation was noticed. A white, slimy precipitate was obtained, which, according to Beilstein, has the composition, $3PbO.C_3H_6O_3$. This was filtered off, washed with alcohol, dried at 100° C., and weighed. The same writer mentions that this precipitate contains 78.5 per cent. lead oxide; therefore there is 21.5 per cent. free lactic acid contained in it. The precipitate in this case weighed 2.595 grams, corresponding to 0.5579 gram of lactic acid.

According to the equation

$$CH_3COCOOH + H_2 = CH_3CH(OH)COOH,$$

10.91 per cent. of the theoretical yield was obtained.

Experiment 2.—Here I used:

Pyroracemic acid	5 grams.
Alcohol	75 cc.
Water	50 cc.
Sodium hydroxide	10 grams.
Temperature	Ordinary.
Time	5 hours.
N. $D._{100}$	0.8 ampere.
Voltage	4 volts.

The cathode liquid was acidulated and treated as above. The precipitate weighed 6.7581 grams, equivalent to 1.4529 grams of lactic acid, or 28.43 per cent. of the theory.

Experiment 3.—The material was:

Pyroracemic acid	5 grams.
Sodium hydroxide	8 grams.
Alcohol	50 cc.
Water	50 cc.
Temperature	50° C.
Time	6 hours.
N. $D._{100}$	0.7 ampere.
Voltage	4 volts.

The cathode liquid under the prescribed treatment yielded 3.9592 grams of precipitate, corresponding to 0.8512 gram lactic acid, equivalent to 16.65 per cent. of theory.

In the preceding experiments platinum electrodes were employed.

Experiment 4.—Lead electrodes were used in this experiment with conditions as follows:

Pyroracemic acid	20 grams.
Sodium hydroxide	10 grams.
Alcohol	100 cc.
Water	110 cc.
Temperature	60° C.
Time	5 hours.
N. $D._{100}$	0.9 ampere.
Voltage	5–6 volts.

The cathode liquid, treated as usual, gave 4.5860 grams of the lead salt, corresponding to 0.9859 gram of lactic acid, equivalent to 9.64 per cent. of theory.

B. Reduction in Sulphuric Acid Solution.

Experiment 1.—Here I used:

Pyroracemic acid	10 grams.
Alcohol	75 cc.
Sulphuric acid (conc.)	20 cc.
Temperature	30° C.
Time	21 hours.
N. $D._{100}$	0.45 ampere.
Voltage	3 volts.

The cathode liquid was directly shaken out with ether, as it was an acid solution, otherwise treatment was the same as when working in an alkaline solution. It yielded 3.0499 grams of the lead salt, corresponding to 0.6557 gram of lactic acid, equivalent to 6.41 per cent. of the theory.

Experiment 2.—The following was used:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	75 cc.
Temperature	30° C.
Time	9 hours.
N. $D._{100}$	0.45 ampere.
Voltage	3 volts.

The cathode liquid gave 7.1718 grams of the lead salt, corresponding to 1.5417 grams of lactic acid, equivalent to 15.08 per cent. of the theory.

Experiment 3.—Here I used:

Pyroracemic acid	5 grams.
Sulphuric acid (conc.)	20 cc.
Alcohol	75 cc.
Temperature	30° C.
Time	6 hours.
N. $D._{100}$	0.6 ampere.
Voltage	$3^1/_3$ volts.

The usual treatment gave 5.3731 grams of the lead salt, corresponding to 1.1552 grams of lactic acid, equivalent to 22.60 per cent. of the theory.

Experiment 4.—Here the following were used:

Pyroracemic acid	5 grams.
Water	50 cc.
Sulphuric acid (conc.)	25 cc.
Alcohol	50 cc.
Time	6 hours.
Temperature	35° C.
N. $D._{100}$	0.8 ampere.
Voltage	$3^1/_3$ volts.

This yielded 6.4670 grams of the lead salt, corresponding to 1.3904 grams of lactic acid, equivalent to 27.19 per cent. of the theory. Platinum electrodes were used in these experiments.

Experiment 5.—Lead electrodes were used in this experiment with the following conditions:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	10 cc.
Alcohol	100 cc.
Temperature	50° C.
Time	$4^1/_2$ hours.
N. $D._{100}$	0.85 ampere.
Voltage	5-6 volts.

The yield was 3.3203 grams of the lead salt, corresponding to 0.7138 gram of lactic acid, equivalent to 6.97 per cent. of the theory.

Experiment 6.—Carbon electrodes were employed here with the following conditions:

Pyroracemic acid	10 grams.
Sulphuric acid (conc.)	15 cc.
Alcohol	100 cc.
Water	50 cc.
Temperature	60° C.
Time	$4^1/_2$ hours.
N. $D._{45}$	0.9 ampere.
Voltage	3.5 volts.

The cathode liquid gave 3.7693 grams of the lead salt, corresponding to 0.8103 gram of lactic acid, equivalent to 7.93 per cent. of the theory.

It might be well to state the maximum and minimum yields of lactic acid.

In alkaline solution under the conditions of experiment (2) the maximum was obtained, under those of (4), the minimum. The figures are 28.43 and 9.64 per cent. of the theoretical yields.

In sulphuric acid solution, under experiment (4), the maximum 27.19 per cent., and under experiment (1), the minimum, 6.41 per cent., of the theoretical was obtained.

In the reduction of pyroracemic acid by electrolytic hydrogen, it seems natural that lactic acid should be the first product of the reduction; also, that by further reduction propionic acid should be obtained.

The latter, in my opinion, is formed at least in small quantities and probably, if exceedingly large quantities of pyroracemic acid were electrolyzed and treated as described, it would be found.

Further, it is noticed in this part also, that the change in the kind of electrodes causes no marked difference.

As a final conclusion it may be stated that this study reveals as products of the electrolytic oxidation and reduction of pyroracemic acid—acetaldehyde, acetic acid, acetic ester, and lactic acid with some probability of diacetyl and propionic acid.

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[CONTRIBUTIONS FROM THE LABORATORIES OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

THE SIGNIFICANCE OF PHOSPHATES IN NATURAL WATERS.

BY A. G. WOODMAN.

Received April 14, 1902.

THE determination of phosphates in a drinking-water is a matter which has not received the attention from water analysts that has been given to the estimation of various other constituents. Any one who looks through the literature cannot help noticing how few are the published results of quantitative estimations of the phosphate content of natural waters, apart from mineral waters. Yet this determination, by reason of the conversion of organic phosphorus compounds into phosphates through the processes of decay, is one which might reasonably be expected to throw considerable light on the question of the pollution of natural waters by objectionable material.

The reasons for this dearth of published data are not far to seek. To be of value the amount of phosphate must be known within rather narrow limits. Qualitative tests are not sufficient. The mere presence of phosphates is by no means definite or even confirmatory evidence of organic pollution. Rocks and minerals containing phosphates are found nearly everywhere and traces, at times even considerable quantities, may be dissolved, especially by waters rich in carbonic acid. This, however, does not constitute a serious objection to the utility of the determination. The same is true of many, if not most, of the constituents upon which reliance is placed in judging of the quality of a water. Unpolluted waters often contain notable amounts of nitrates and chlorides and a true judgment can be rendered only after comparison with samples from adjacent but unpolluted sources.

The chief reason, however, has been the lack of an accurate and simple method, sufficiently delicate, and of enough data to work out a standard for comparison. It is even declared, with some authority, that the determination is entirely worthless. Wanklyn says of it:[1] "Much nonsense has been talked about phosphates in drinking-water; and the fact has been overlooked that, except as

[1] "Water Analysis," p. 109 (1891).

infinitesimal traces, they cannot exist along with carbonate of lime in a clear water." And at a later date Thresh remarks:[1] "The difficulty of detecting phosphates, when silica is also present, as is usually the case, the still greater difficulty of estimating the quantity, and the very doubtful value of the information when obtained, has caused most chemists to ignore their presence. Traces may be found in wholesome waters, and their absence affords no proof that a water is free from pollution, hence the determination is useless."

That, in spite of Wanklyn's statement to the contrary, appreciable quantities of phosphates may exist in natural waters along with carbonate of lime, has been shown by Hehner.[2] It is pointed out that, theoretically, from the established solubility of calcium phosphate a water may contain 36.6 parts of phosphorus pentoxide per million; and that water saturated with carbon dioxide, a condition which frequently does exist, may hold in solution as much as 67.5 parts of phosphorus pentoxide in a million, which is quite as large an amount as is the case with several of the mineral constituents usually determined. In an actual case cited the amount of phosphate found was 5.5 parts phosphorus pentoxide per million, and Harvey[3] found 14.7 parts in a well water from the chalk formation.

The second objection, the lack of a simple and accurate process of estimation, is no longer valid since the former gravimetric methods, which were tedious and introduced the liability to serious error in concentrating large volumes of water, have been replaced by colorimetric methods. The colorimetric processes, which are based in general upon the reaction with alkali molybdates, as proposed in 1880 by J. West-Knights[4] and later improved by Lepierre[5] and by Jolles and Neurath,[6] have been critically studied in this laboratory[7] and the method finally adopted seems to solve the problem in a satisfactory manner. The method as applied to colorless waters, for which it is best suited, may, for convenience, be briefly repeated here.

[1] "Water Supplies," p. 170 (1896).
[2] *Analyst*, **5**, 135 (1880).
[3] *Ibid.*, p. 197.
[4] *Ibid.*, **5**, 197 (1880).
[5] *Bull. Soc. Chim.*, **15**, 1213 (1896).
[6] *Monatsh. Chem.*, **19**, 5 (1898).
[7] Woodman and Cayvan: This Journal, **23**, 96 (1901).

Fifty cc. of the water and 3 cc. of nitric acid (sp. gr. 1.07) are evaporated to dryness in a 3-inch porcelain dish on a water-bath. The residue is heated in an oven for two hours at the temperature of boiling water. The dry residue is then treated with 50 cc. of cold distilled water, added in several portions, and poured into the comparison tube. It is not necessary to filter the solution. Four cc. of ammonium molybdate (50 grams per liter) and 2 cc. of nitric acid are added, the contents of the tube mixed, and the color compared, after three minutes, with standards made by diluting varying quantities of the standard phosphate solution (1 cc. = 0.0001 gram phosphorus pentoxide) to 50 cc., and adding the reagents as above. A blank should always be made on the distilled water used for dilution, especially if it has stood for any length of time in glass vessels.

The method as outlined has been used on a number of waters from various sources which have been examined from time to time and the results, together with the figures for the other important determinations usually made are given in the accompanying tables. For convenience they are divided roughly into three classes: waters which may fairly be considered unpolluted; samples of doubtful purity; waters plainly polluted. This classification is based on the amounts of the other constituents rather than on the quantity of phosphate in order to determine the valuation and limits of the latter. Table IV gives the results of analysis of several samples from the same general source, showing the correspondence of the various constituents under varying conditions. The results are given in all cases in parts per million.

On examining the results it will be observed that the amount of phosphate shows considerable variations for a given class of waters, which might indeed well be expected when we take into consideration the readiness with which it is absorbed or precipitated. It has been found too, that it seems to be more or less dependent upon the amount of iron, an instance of which will be found in No. 20 of Table III; a part of the phosphate has been removed, no doubt, by sedimentation as ferric phosphate.

In Table I samples 2 and 3 had been standing in the collecting bottles for some time before being analyzed, which would have a tendency to make the results too high. Sample 9 is interesting by comparison with a sample from the same source (III, 8) taken

TABLE I.—UNPOLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Southboro, Mass	....	0.008	0.060	0.000	0.000	1.8	11.1	0.90	Spring in the woods.
2	Newburyport, Mass....	50.0	0.002	0.024	0.001	0.400	9.2	....	2.7	City supply—driven wells.
3	Belmont, Mass	....	0.006	0.008	0.001	0.500	3.29	....	1.7	Spring.
4	Lowell, Mass.....	102.0	0.012	0.046	0.000	0.400	2.7	....	0.54	City supply.
5	Winsted, Conn.....	31.5	0.017	0.020	0.000	0.000	4.2	....	0.44	Spring—no contamination.
6	Poughkeepsie, N. Y...	....	0.003	0.010	0.002	1.250	5.8	....	0.4	Purified water.
7	Dublin, N. H.....	....	0.006	0.016	0.000	0.000	1.6	8.0	0.08	
8	Dublin, N. H.....	....	0.008	0.006	0.000	0.080	0.8	9.0	0.14	
9	Jamaica Pond, Mass...	....	0.014	0.406	0.000	0.000	8.0	....	0.20	Heavy growth of organisms —*Oscillatoria prolifica.*
10	Marion, Mass	....	0.004	0.120	0.000	0.600	94.0	....	0.70	Near salt water.
11	Marion, Mass	....	0.002	0.002	0.008	0.400	11.2	30.9	0.80	Artesian well.
12	Marion, Mass	....	0.000	0.024	0.000	0.150	12.0	55.0	0.14	Milky with clay.
13	Bedford, Mass	....	0.002	0.008	0.000	0.100	3.0	38.0	0.80	
14	Essex, Mass	....	0.018	0.070	0.001	0.350	7.0	21.0	0.0	Cistern, unpolluted.
15	Essex, Mass	85.0	....	0.096	....	0.560	10.5	....	0.54	Spring near tide-water.

TABLE II.—DOUBTFUL WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Canton, Mass	....	0.002	0.032	....	1.600	40.0	....	0.4	
2	Canton, Mass.....	61.0	0.005	0.024	0.000	1.600	7.2	....	1.6	
3	Winsted, Conn.....	200.0	0.240	0.070	0.019	4.900	25.4	....	0.26	
4	Cambridge, Mass.....	116.0	0.004	0.032	0.000	3.000	8.24	....	1.8	
5	Essex, Mass.....	214.0	0.000	0.052	0.002	4.500	16.0	...	3.0	Pump and watering trough near road.
6	Canaan, N. H.....	....	0.086	0.154	0.015	2.500	4.0	....	1.6	
7	Canaan, N. H.....	....	0.012	0.068	0.000	2.000	4.0	....	1.6	
8	Bedford, Mass.....	72.5	0.000	0.012	0.003	1.100	4.4	26.0	0.80	Milky with clay.
9	Jamaica Plain, Mass....	109.5	0.032	0.002	0.000	2.000	12.0	47.0	0.60	On hill—few houses near.
10	Boxford, Mass.....	....	0.000	0.032	0.000	0.900	6.0	61.0	1.2	Well near road.
11	Boxford, Mass.....	....	0.000	0.024	0.000	1.900	2.5	20.0	1.8	Well at foot of hill.
12	Hopkinton, Mass.....	. ..	0.004	0.000	0.000	0.450	4.8	....	2.2	
13	Essex, Mass.....	....	0.014	0.092	0.000	0.560	....	41.6	1.4	Well in pasture.
14	Mattapoisett, Mass.....	....	0.004	0.026	0.016	1.850	19.0	41.6	0.4	
15	Wenham, Mass.....	188.0	0.008	0.106	0.030	0.500	10.8	....	1.7	

TABLE III.—POLLUTED WATERS.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Newburyport, Mass...	322.5	0.026	0.090	0.008	42.5	57.1	....	3.6	
2	Beverly, Mass.....	227.0	....	0.028	0.001	16.000	20.1	....	3.8	
3	Everett, Mass.....	....	0.008	0.018	0.004	19.000	26.1	....	6.8	Spring water sold in city.
4	Essex, Mass.....	....	0.010	0.050	0.010	10.000	36.7	....	8.6	Town pump.
5	Framingham, Mass...	691.0	0.930	0.080	0.010	50.000	72.2	....	3.8	Well in barnyard.
6	Newburyport, Mass...	88.0	0.010	0.016	0.000	7.000	20.4	....	1.8	Driven well.
7	Canton, Mass.....	...	0.000	0.034	0.000	11.000	46.1	....	3.8	
8	Jamaica Pond, Mass...	67.5	0.010	0.134	0.003	0.220	8.4	....	3.7	Pond practically free from *Oscillatoria*.
9	Essex, Mass	200.0	0.000	0.036	0.000	2.250	32.5	....	8.0	Well near the house.
10	Poughkeepsie, N. Y...	20.6	0.013	0.150	0.006	1.750	5.2	....	1.4	Brook contaminated by sewage effluent.
11	Poughkeepsie, N. Y...	21.3	0.029	0.140	0.011	0.600	11.3	....	3.8	Brook contaminated by sewage effluent.
12	Poughkeepsie, N. Y...	....	0.004	0.046	0.010	6.500	25.1	....	9.0	Brook contaminated by sewage effluent.
13	Bedford, Mass.....	203.0	0.004	0.108	0.000	5.500	6.7	57.0	1.4	
14	Canaan, N. H.....	....	0.006	0.112	0.002	15.000	32.0	110.0	4.0	
15	Long Island, N. Y....	836.0	0.006	0.036	0.003	34.000	80.0	400.0	3.2	Artesian well.
16	Newport, R. I.....	142.0	0.008	0.026	0.001	3.750	16.0	46.0	2.0	
17	Annisquam, Mass.....	....	0.014	0.006	0.000	2.250	35.0	38.0	2.4	
18	W. Falmouth, Mass...	....	0.084	0.100	0.010	4.500	38.0	43.0	2.4	
19	Essex, Mass.....	....	0.014	0.054	0.002	8.330	41.0	104.5	13.3	Well—large henyard on slope above.
20	Natick, Mass.....	....	0.120	0.080	0.022	16.600	47.8	....	2.6	Sewage effluent—high in iron.

20	Natick, Mass.....	....	0.120	0.080	0.022	16.600	47.8	....	2.6	Sewage effluent—high in iron.

TABLE III.—POLLUTED WATERS (*Continued*).

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
21	Malden, Mass.....	....	0.000	0.016	0.002	7.500	60.8	81.4	7.4	Well surrounded by drains and cesspools.
22	Canton, Mass.....	113.0	0.000	0.038	0.000	3.500	23.5	36.2	5.0	Used only for garden.
23	Newport, R. I.....	....	0.248	0.068	0.500	8.500	83.0	121.1	4.6	Typhoid fever among families using this well.
24	Marblehead, Mass....	360.0	0.000	0.080	0.018	7.500	47.0	140.4	5.6	Surrounded by houses.
25	Marblehead, Mass....	600.0	0.000	0.080	0.008	10.000	56.0	264.5	6.8	Surrounded by houses.
26	Thompson, Conn.....	....	0.000	0.008	0.000	1.850	4.04	42.9	6.6	
27	Thompson, Conn.....	...	0.042	0.046	0.000	2.450	1.04	20.8	3.6	
28	Essex, Mass.....	235.0	0.008	0.040	0.000	3.500	16.6	74.3	4.7	
29	Essex, Mass.....	520.0	0.016	0.088	0 001	5.250	90.6	205.6	7.6	Sink drain within 4 feet of well.
30	Boxford, Mass.....	....	0.002	0.032	0.000	20.000	24.1	132.0	4.8	Well about 50 feet from barn.
31	Dartmouth, Mass.....	....	0.000	0.008	0.000	2.850	8.2	27.3	3.3	
32	Hopkinton, Mass.....	....	0.006	0.004	0.008	7.000	5.9	....	5.4	
33	So. Essex, Mass.....	409.0	0.050	0.078	0.007	7.500	93.8	151.4	4.2	Well between house and barn.
34	So. Essex, Mass.....	290.0	0.116	0.130	0.004	11.200	37.3	180.2	4.9	Well in yard near house.
35	Essex, Mass.....	....	0.000	0.012	0.000	3.050	40.6	60.0	6.0	Spring on slope from cemetery.
36	W. Falmouth, Mass..	169.0	0.000	0.026	0.000	4.500	39.0	45.7	4.0	
37	Stoneham, Mass.....	....	0.082	0.028	0.001	24.000	14.0	125.6	3.2	Spring, cesspool found beside it.
38	Southboro, Mass.....	124.0	0.000	0.000	0.000	3.000	10.0	....	4.0	Well in pasture.
39	Jamaica Plain, Mass..	....	0.010	0.030	0.001	4.250	30.8	114.3	6.6	Well in cellar of house.
40	Jamaica Plain, Mass..	....	0.000	0.028	0.000	4.000	19.2	70.7	4.9	21 feet deep, near house.
41	Jamaica Plain, Mass..	....	0.010	0.024	0.000	4.000	20.2	71.3	4.6	108 feet deep, in barnyard.
42	Cambridge, Mass.....	....	0.034	0.028	0.160	19.000	17.5	126.0	1.3	

TABLE IV.

No.	Locality.	Residue.	Free ammonia.	Albuminoid ammonia.	Nitrites.	Nitrates.	Chlorine.	Hardness.	Phosphorus pentoxide.	Remarks.
1	Sayre, Pa	266.0	0.001	0.018	0.001	1.500	9.7	183.4	2.9	Supply well after pumping out six times.
2	Sayre, Pa	293.0	0.000	0.000	0.000	1.600	12.4	196.6	3.1	Pump in driven well back of station.
3	Sayre, Pa	121.0	0.018	0.042	0.000	0.120	5.0	79.4	0.70	River at "intake."
4	Sayre, Pa	257.0	0.000	0.006	0.001	1.500	9.8	182.8	3.1	Supply well after pumping out nine times.
5	Sayre, Pa	106.0	0.005	0.058	0.000	0.070	4.4	76.8	0.70	House faucet from tap in town.
6	Sayre, Pa	258.0	0.000	0.022	0.001	1.440	9.7	182.8	3.1	Supply well after pumping out three times.

under different conditions, as showing the change in phosphate content through the increase of organic life.

The amount of phosphate and its variation seem to follow the same general line as the other mineral constituents which either accompany the polluting material or are produced by its decay, especially the nitrates and chlorides. It is not, however, so delicate an indicator as these. This correspondence is well shown in the samples in Table IV and also in samples 10 to 12 of Table III, where the increased pollution, as evidenced by the gradual increase in chlorine, is accompanied by increased phosphate.

The results obtained by the colorimetric method would seem to indicate that the limit of 0.5 part of phosphorus pentoxide in a million, as given by Hehner for unpolluted waters, is rather low. A safer amount would be 1.0 part, although the average would doubtless be lower than this.

The highest amount found was 13.3 parts, in sample 19 of Table III. The same rather surprising cases were found as noticed by Hehner in which the amount of phosphate is very much lower than would be expected from the source of the water and the other constituents determined, which may be due to the character of the soil through which the water has percolated. Even with all the drawbacks which are noted there can be no question, in view of the figures given above, that the presence of phosphates in a water in any quantity is significant of pollution, and the determination must be considered as another link (of which we have none too many, anyway) in the chain of circumstantial evidence by which we are often compelled to judge the purity of a water.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(FIFTH PAPER.)

BY HENRY L. WHEELER AND GEORGE S. JAMIESON.

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IN this paper we describe a number of exceptions to the rule that the only halogen compounds which undergo any material

conversion into isothiocyanate, by acting on potassium thiocyanate in benzene or alcoholic solutions, are those in which the halogen is in direct combination with a negative group, as in the case of the acyl halides.[1] This rule, until recently, was supposed to be general for all except the allyl halides. The formation of isothiocyanates by the latter had already been ascribed to the negative character of the allyl group.[2]

The view that a strong negative character favors the formation of isothiocyanates appears to be supported by the fact that 2,4-dinitrochlorbenzene gives a normal thiocyanate, $C_6H_3(NO_2)_2SCN$, while 2,4,6-trinitrobenzene gives an isothiocyanate, $C_6H_2(NO_2)_3NCS$.[3]

In the first paper[4] of this series it was shown that certain more or less negative halogen compounds, which were supposed to give isothiocyanates, in reality give nothing but normal thiocyanates. In the second[5] the combined influence of several negative groups together was considered, and it was found that when two hydrogen atoms in methyl bromide were replaced by two phenyl groups another exception to the above rule resulted. Diphenylmethyl bromide was found to give an isothiocyanate. The presence of three phenyl groups, on the other hand, and also of one, two, or three carboxyl groups, did not confer on the substituted methyl halide the property of forming isothiocyanate.

The third paper[6] dealt with dirhodanides, but no isothiocyanates, were observed in these cases.

In the fourth[7] a series of tertiary halides were examined and here again no exceptions to the above rule were found.

From these results, especially those in the second paper, it would seem that the tendency to form isothiocyanate is not dependent on, or proportional to, the negative character of the halide, for it would seem probable that triphenylmethyl bromide is a more negative halide than diphenylmethyl bromide, and di- and tricarbethoxymethyl bromide more negative than the latter. This, as already pointed out, is indicated by comparing the affinity-

[1] Dixon: *J. Chem. Soc.* (London), **75**, 390 (1899).
[2] Michael: *J. prakt. Chem.*, **37**, 509 (1888).
[3] Crocker: *J. Chem. Soc.* (London), **81**, 436 (1902).
[4] This Journal, **23**, 283 (1901).
[5] *Am. Chem. J.*, **26**, 345 (1901).
[6] This Journal, **24**, 439.
[7] *Ibid.*, **24**, 680.

constants of acids that contain these groups. It must be remarked, however, that Vorländer,[1] in his interesting paper "Ueber die Natur der Radicale," calls attention to the fact that this method of deciding negative character can not be relied upon.

The work done in this laboratory has also shown that of the twenty possible halides which can be formed by substituting the three groups, $-CH_3$, $-C_6H_5$, and $-CO_2C_2H_5$, for hydrogen in methyl bromide, only one of these, namely, diphenylmethyl bromide, gives an isothiocyanate. It appears now that this unique behavior is general in the case of those substituted methyl bromides which contain two aromatic radicals.

We have found that phenyl-α-naphthylmethyl and di-α-naphthylmethyl bromides give isothiocyanates. Phenylparatolylmethyl bromide, $C_6H_5CHBrC_6H_4CH_3$, from the carbinol and hydrogen bromide, also gives an isothiocyanate, while, on the other hand, the isomeric halide, parabenzyl-1'-bromtoluene, $C_6H_5CH_2C_6H_4CH_2Br$, forms a normal thiocyanate.

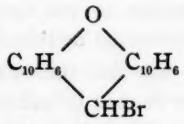
That the rhodanides are isothiocyanates follows from the fact that they react at ordinary temperature with amines yielding thioureas, and also, from their action with thioacetic and thiobenzoic acids, when carbon disulphide is evolved and substituted amides are formed.

The fact that the above bromides react with potassium thiocyanate, and the ease with which the isothiocyanates react with amines (especially β-naphthylamine) to form difficultly soluble ureas, afford an easy test for the position of halogens in the homologues and analogues of diphenylmethane. For example, on brominating p-benzyltoluene at 130°-135°, and converting the product into rhodanide, it was easy by means of β-naphthylamine to show that phenylparatolylmethyl bromide had been formed, or in other words, that hydrogen in the CH_2 group had been substituted. According to Senff[2] the corresponding metabenzyltoluene is attacked only in the CH_3 group.

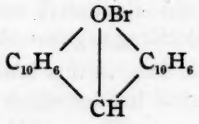
Again, if, as formerly considered, the bromxanthenes, bromdinaphtoxanthene, etc., have the structure represented by Formula I, it might be expected that they would yield isothiocyanates, while

[1] *Ann. Chem.* (Liebig), **320**, 99 (1902).
[2] *Ibid.*, **220**, 240 (1883).

according to the latest representation,[1] II, they probably would not.



I.

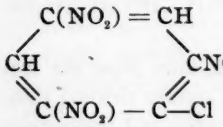


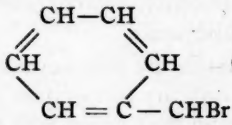
II.

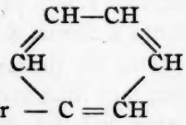
A qualitative test with β-naphthylamine, in fact, after boiling the bromide in chloroform with potassium thiocyanate, failed to give any evidence of the formation of an isothiocyanate.

If the aryl groups are given Kekulé's formula, then the alkyl halides which have thus far been found to give isothiocyanates have one common property. There is either a double bond or at least an unsaturated condition in the 2,3-position:

$$CH_2 = CH - CH_2I,$$







A similar condition, nevertheless, exists in 2,4-dinitrochlorbenzene and in 1'-bromethylbenzene, in brommalonic ester and in the α-halogen acid derivatives, $ClCH_2CO.R$, in general; but none of these halides gives isothiocyanate. This would seem to indicate that a sufficiently negative character as well as an unsaturated condition is required for the formation of isothiocyanates. In how far this idea is applicable and what other influences are at work, cannot be judged from the few data at hand.

EXPERIMENTAL PART.

Phenylparatolylmethylbromide, $C_6H_5CHBrC_6H_4CH_3$.—Phenylparatolyl carbinol was heated to 100° in a stream of dry hydrogen bromide, whereupon water was evolved and the required increase in weight took place. The product, a thin red oil, was then dried in a vacuum at 100° for analysis. A bromine determination gave:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	30.40

This bromide refused to solidify in a freezing-mixture or on

[1] Werner: *Ber. d. chem. Ges.*, **34**, 3303 (1901); Posse: *Compt. rend.*, **133**, 101 (1901); **134**, 64 (1502).

standing exposed to the air for over three weeks. No attempt was made to distil the oil since diphenylmethyl bromide is decomposed by this treatment even in a vacuum.

Phenylparatolylmethylisothiocyanate, $C_6H_5CH(NCS)C_6H_4CH_3$, was obtained by heating a benzene solution of the bromide with potassium thiocyanate for two days. The product was a thin reddish colored oil, the vapor of which, especially when warmed, had an irritating action on the eyes. A nitrogen determination gave:

	Calculated for $C_{15}H_{13}NS$.	Found.
Nitrogen	5.85	5.72

Phenylparatolylmethylacetamide, $C_6H_5(CH_3C_6H_4)CHNHCOCH_3$.—Two grams of the isothiocyanate, 1.5 grams of thioacetic acid and 2 volumes of benzene were heated somewhat over two hours on the steam-bath. On evaporating the benzene, carbon disulphide was found in quantity, and the residue taken up in ether, washed with alkali and water, gave colorless, flat, rectangular prisms, on evaporating the solvent. This amide is soluble in hot water but on cooling it separates as an oil. For analysis it was crystallized from ether, whereupon it melted at 129.5°-131°, and a nitrogen determination of the sulphur-free material gave:

	Calculated for $C_{16}H_{17}ON$.	Found.
Nitrogen	5.85	6.12

Phenylparatolylmethylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNH_2$, was obtained by dissolving the isothiocyanate in alcoholic ammonia. It separated from alcohol in clusters or balls of colorless needles which melted at 162°-163° and gave the following result on analysis:

	Calculated for $C_{15}H_{16}N_2S$.	Found.
Nitrogen	10.93	11.13

Phenylparatolylmethylphenylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_6H_5$.—The isothiocyanate reacted immediately with aniline. The product formed colorless, flat prisms from alcohol, which melted at 159°. A nitrogen determination gave:

	Calculated for $C_{21}H_{20}N_2S$.	Found.
Nitrogen	8.4	8.5

Phenylparatolylmethyl-β-naphthylthiourea, $C_6H_5(CH_3C_6H_4)CHNHCSNHC_{10}H_7$, forms as a precipitate when alcoholic solutions of the rhodanide and β-naphthylamine are mixed. It crystallizes from alcohol in bunches of slender, colorless needles melting at 170°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.73	7.70

The Bromination of Parabenzyltoluene.—The hydrocarbon was brominated at 130°-135° and the product was distilled at 11 mm. pressure, whereupon it boiled quite constantly at 179°-180°. It formed a heavy, pale yellow oil. The amount of replaceable bromine was determined by means of sodium ethylate:

	Calculated for $C_{14}H_{13}Br$.	Found.
Bromine	30.65	27.74

The brominated material was heated with potassium thiocyanate in benzene solution for two days. An oil was thus obtained which responded to the reduction test for a normal thiocyanate. A nitrogen determination gave 5.18 per cent. nitrogen instead of 5.85 per cent. An alcoholic solution was allowed to stand with β-naphthylamine, and one with ammonia. In both cases a small amount of crystals was obtained which were identical with the corresponding ureas described above from phenylparatolylisothiocyanate prepared from the carbinol. This shows that on brominating benzyltoluene a portion of the bromine enters the CH_2 group.

Phenyl-α-naphthylmethylbromide, $C_6H_5(C_{10}H_7)CHBr$.—Miquel[1] obtained this bromide by brominating α-benzylnaphthalene, either hot or cold or in carbon disulphide solution. He found that it was a syrup. Our material was prepared by brominating the hydrocarbon at 140°-150°, under the same conditions as the crystalline diphenylmethyl bromide is obtained.[2] The product formed a dark red oil which was dried over potash for analysis. The amount of replaceable bromine was then determined by warming a sample with sodium ethylate:

	Calculated for $C_{17}H_{13}Br$.	Found.
Bromine	26.9	24.6

[1] *Bull. Soc. Chim.* [2], **26**, 4 (1876).

[2] Friedel, Balsohn: *Bull. Soc. Chim.*, **33**, 339.

Phenyl-α-naphthylmethylisothiocyanate,
$C_6H_5(C_{10}H_7)CHNCS$.—A benzene solution of the bromide was heated for forty-eight hours with potassium thiocyanate. On filtering and evaporating the benzene a thick red oil was obtained which deposited nothing solid on cooling. An attempt to purify a portion by distilling under reduced pressure resulted in complete decomposition of the material, some naphthylphenylmethane being obtained. A portion was treated with alcohol and sodium, whereupon it was found that sodium cyanide and thiocyanate were formed. This indicates the presence of normal thiocyanate. The crude oil was dried in a vacuum for analysis and a nitrogen determination then gave:

	Calculated for $C_{18}H_{13}NS$.	Found.
Nitrogen	5.09	4.27

When a portion of this oil was allowed to stand for about six months it solidified. It then formed small plates, from petroleum ether, melting at 76°-77°.

Phenyl-α-naphthylmethylacetamide,
$C_6H_5(C_{10}H_7)CHNHCOCH_3$.—Ten grams of the crude isothiocyanate, in benzene solution, were mixed with 2.8 grams of thioacetic acid and heated upon the steam-bath for three hours. Carbon disulphide was evolved and the acetamide separated on cooling the solution. When crystallized from toluene and some alcohol, small needles were obtained which melted at about 210°. A nitrogen determination gave:

	Calculated for $C_{19}H_{17}ON$.	Found.
Nitrogen	5.09	5.23

Phenyl-α-naphthylmethylbenzamide,
$C_6H_5(C_{10}H_7)CHNHCOC_6H_5$.—Ten grams of the rhodanide were heated for an hour with the calculated amount of thiobenzoic acid. On evaporating the benzene, carbon disulphide was found in quantity by the xanthate test. The benzamide was crystallized from alcohol; it then melted at 158° and a nitrogen determination in the sulphur-free material gave:

	Calculated for $C_{24}H_{19}ON$.	Found.
Nitrogen	4.15	4.11

Phenyl-α naphthylmethylthiourea,
$C_6H_5(C_{10}H_7)CHNHCSNH_2$.—A solution of the isothiocyanate

in alcoholic ammonia was obtained and in a half hour, radiating masses of flat rectangular prisms separated. They were crystallized from alcohol and melted at 197°-198°. A nitrogen determination gave:

	Calculated for $C_{18}H_{16}N_2S$.	Found.
Nitrogen	9.58	9.59

This thiourea is insoluble in water and very difficultly soluble in 20 per cent. sodium hydroxide.

Phenyl-α-naphthylmethylmethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHCH_3$.—Three grams of the isothiocyanate were dissolved in alcohol and an excess of a 33 per cent. solution of methylamine was added. After standing some time small prisms arranged in clusters separated. They were crystallized from alcohol and melted at 175°-176°. A nitrogen determination gave:

	Calculated for $C_{19}H_{18}N_2S$.	Found.
Nitrogen	9.1	8.8

Phenyl-α-naphthylmethyldiethylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_2H_5)_2$, from the isothiocyanate and diethylamine, formed clusters of flat prisms or a sandy powder. It melted at 112°-113° and a nitrogen determination gave:

	Calculated for $C_{22}H_{24}N_2S$.	Found.
Nitrogen	8.04	8.00

Phenyl-α-naphthylmethyldiisobutylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(C_4H_9)_2$, formed clusters of slender radiating crystals from alcohol melting at 142°-143°. A nitrogen determination gave:

	Calculated for $C_{26}H_{32}N_2S$.	Found.
Nitrogen	6.93	7.22

Phenyl-α-naphthylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_5$, formed a difficultly soluble precipitate when the constituents were mixed in benzene. It was crystallized from a mixture of toluene and ethyl benzoate, whereupon colorless prisms melting at 185° were obtained. A nitrogen determination gave:

	Calculated for $C_{24}H_{20}N_2S$.	Found.
Nitrogen	7.60	7.64

Phenyl-α-naphthylmethylmethylphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSN(CH_3)C_6H_5$, formed a fine, white crystalline powder which, on crystallizing from toluene, melted at 182°-183°. A nitrogen determination gave:

	Calculated for $C_{25}H_{22}N_2S$.	Found.
Nitrogen	7.32	7.35

Phenyl-α-naphthylmethylmetachlorphenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4Cl$, formed colorless, needle-like prisms from alcohol, melting at 172°-173°. A nitrogen determination gave:

	Calculated for $C_{24}H_{19}N_2ClS$.	Found.
Nitrogen	6.95	6.93

Phenyl-α-naphthylmethylmetanitrophenylthiourea, $C_6H_5(C_{10}H_7)CHNHCSNHC_6H_4NO_2$, was difficultly soluble in alcohol from which it crystallized in the form of light yellow prisms. It melted at 191°, and a nitrogen determination gave:

	Calculated for $C_{24}H_{19}O_2N_3S$.	Found.
Nitrogen	10.17	10.10

Phenyl-α-naphthylmethyl-β-naphthylthiourea, $C_6H_5(C_{10}H_7)CH—NHCSNHC_{10}H_7$, gave colorless needles from toluene melting at 195°. A nitrogen determination gave:

	Calculated for $C_{28}H_{22}N_2S$.	Found.
Nitrogen	6.69	6.52

Phenyl-α-naphthylmethylphenylthiosemicarbazide was obtained from the isothiocyanate and phenylhydrazine in an alcoholic solution. Thus obtained, it melted at about 154°, solidified, and melted then at 174°-175°, with decomposition and effervescence. A recrystallization from alcohol gave needles which melted at 178°-179°. Evidently we have to deal here with a molecular rearrangement similar to that observed by Busch and Holzmann:[1]

$C_6H_5(C_{10}H_7)CHNHCS(C_6H_5)N—NH_2$ ➙
Melting-point 154°.

$C_6H_5(C_{10}H_7)CHNHCSNH—NHC_6H_5$.
Melting-point 178°-179°.

An analysis of the material crystallized from alcohol gave:

	Calculated for $C_{24}H_{21}N_3S$.	Found.
Nitrogen	11.32	11.30

[1] *Ber. d. chem. Ges.*, **34**, 320 (1901).

Di-α-naphthylmethane, $(C_{10}H_7)_2CH_2$.—The onlymethod given in Beilstein's "Handbuch" for the preparation of this hydrocarbon is that of Grabowski.[1] This method, according to our experience, gives a very poor yield (4 to 6 per cent.). By far the largest portion of the naphthalene in this process is converted into a difficultly soluble substance, the nature of which we did not stop to determine.

By means of the following method we have obtained yields over twice as great a by the above and with much less trouble.

Twenty-three grams of chlormethylacetate, CH_3COOCH_2Cl, 60 grams of naphthalene and 15 grams of fused zinc chloride (powdered) were mixed and heated on the steam-bath until the evolution of hydrogen chloride practically ceased. This required about three hours. The product was then washed with water, taken up with ether, and dried over calcium chloride. The ether was removed and all that came over below 300° was discarded. From this point the distillation was carried on as long as possible. The product above 300° was then distilled at 14 mm. pressure, whereupon most of the material boiled at 270°-272°. It had a strong blue fluorescence by reflected light and on standing a few hours it solidified. On crystallizing from alcohol 7 grams of the hydrocarbon were obtained melting at 99°-100°.

Di-α-naphthylmethylbromide, $(C_{10}H_7)_2CHBr$, was prepared from the hydrocarbon, obtained by both of the above methods, by brominating at 135°-145°. The bromide crystallized from benzene in needle-like prisms which melted at 181°-182°. It was very soluble in chloroform and sparingly soluble in ligroïn. A bromine determination gave:

	Calculated for $C_{21}H_{15}Br$.	Found.
Bromine	23.0	22.9

Di-α-naphthylmethylisothiocyanate, $(C_{10}H_7)_2CHNCS$. — The bromide was boiled in benzene with potassium thiocyanate for three days. The product, an oil, solidified on standing. It was then crystallized from alcohol and obtained in the form of colorless rectangular prisms, which melted at 124°-125°. A nitrogen determination gave:

	Calculated for $C_{22}H_{15}NS$.	Found.
Nitrogen	4.30	4.30

[1] *Ber. d. chem. Ges.*, **7**, 1605.

Di-α-naphthylmethylphenylthiourea, $(C_{10}H_7)_2CH—NHCSNHC_6H_5$, from the above rhodanide and aniline, when crystallized from ethyl benzoate, gave colorless needles melting at 225°-226°. It was only sparingly soluble in toluene and amyl acetate. A nitrogen determination gave:

	Calculated for $C_{29}H_{22}N_2S$.	Found.
Nitrogen	6.69	6.53

Di-α-naphthylmethylmethylphenylthiourea, $(C_{10}H_7)_2CH—NHCSN(CH_3)C_6H_5$, from the isothiocyanate and methyl aniline, crystallized from toluene in fine colorless needles melting at 210°-211°. A nitrogen determination gave:

	Calculated for $C_{30}H_{24}N_2S$.	Found.
Nitrogen	6.48	6.59

Di-α-naphthylmethyl-β-naphthylthiourea, $(C_{10}H_7)_2CH—NHCSNHC_{10}H_7$, separated in balls of needles from the alcoholic solution of its constituents. It crystallized from amyl acetate and melted at 218°-219°. A nitrogen determination gave:

	Calculated for $C_{32}H_{24}N_2S$.	Found.
Nitrogen	5.98	6.11

The following rhodanides were examined in order to complete the list of twenty compounds mentioned in the introduction.

1'-Thiocyanethylbenzene and Thioacetic Acid.—This thiocyanate, which may be viewed as methylphenylmethyl rhodanide, $CH_3(C_6H_5)CHSCN$, reacted smoothly with thioacetic acid and the product crystallized from alcohol, in which it was very soluble, in slender yellow prisms. It melted at 99°-100° and was soluble in alkali from which solutions acids precipitated the material unaltered. These properties and the following nitrogen determination show that this substance is an acetyldithiourethane, namely, $CH_3CONHCS.SCH(CH_3)C_6H_5$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen	5.85	6.16

Isopropyl Thiocyanate and Thiobenzoic Acid.—Four grams of isopropyl thiocyanate and 5.4 grams of the acid were dissolved in 2 volumes of benzene and heated several hours on the steam-bath. On cooling, brilliant yellow plates separated. They were recrystallized from alcohol and melted at 74°-75°. The material was

soluble in alkali and was reprecipitated unaltered by acids. A nitrogen determination agreed with the calculated for *benzoyldithioisopropyl carbamate,* $C_6H_5CONHCS.SC_3H_7$.

	Calculated for $C_{11}H_{13}ONS_2$.	Found.
Nitrogen.....	6.11	6.08

These latter rhodanides are therefore both normal thiocyanates.

NEW HAVEN, CONN.,
April 12, 1902

[CONTRIBUTIONS FROM THE BUREAU OF CHEMISTRY U. S. DEPARTMENT OF AGRICULTURE, NO. 45. SENT BY H. W. WILEY.]

REFRACTIVE INDICES OF SALAD OILS—CORRECTION FOR TEMPERATURE.

BY L. M. TOLMAN AND L. S. MUNSON.

Received April 28, 1902.

IT IS almost always difficult to obtain exactly a definite temperature at which to make readings of refractive indices. A method and factor for making exact correction for this variation and also for making possible recalculations of determinations made at different temperatures is desirable.

Two factors are ordinarily used in this country to make this correction. One, 0.000176[1] for 1° C. for instruments reading index of refraction directly, and 0.55 scale division for 1° C. for the Zeiss butyrorefractometer, which has an empirical scale. As will be seen later, the former is considerably too small, and the latter was determined for butter-fat and is not correct for oils which have higher refractive indices.

As the butyrorefractometer is very largely used in this country, special attention should be called to a satisfactory method for correcting its readings for temperature. It must be remembered, however, that this discussion is limited to oils, and to the very limited number of oils given in Table III. Other substances and oils vary, and require different corrections for temperature. This instrument on account of its simplicity, ease of manipulation, and water jacket has acquired a very wide use but its empirical scale with division of varying value in refractive indices makes correction for temperature difficult and not exact unless, as is shown

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 334.

later, the scale readings are calculated to refractive indices and the correction factor applied to that, and then the corrected refractive index recalculated to scale division.

Table I[1] illustrates this variation of value of scale division in index of refraction.

TABLE I.

Scale division.	N.D.	Difference.
0	1.4220	0.0080
10	1.4300	
40	1.4524	0.0069
50	1.4593	
90	1.4840	0.0055
100	1.4895	

Ten scale divisions from 0 to 10 equal 0.008 in index of refraction while from 90° to 100° they equal 0.0055. From this it is evident that if, as shown from Table III, the change in refractive index for 1° C. is practically a constant, then the change in scale division for 1° C. must be a variable.

Taking from Table III the average change in refractive index for 1° C. 0.000365, we find that it equals 0.46 of a scale division on reading from 0 to 10 on the scale and 0.66 of a scale division from 90° to 100° on the scale. Therefore on oils or fats, other things being equal, those that have a low reading will have a lower correction for temperature in scale divisions than those that have a high reading. This is illustrated in Table II, from readings made on a rape oil.

TABLE II.

Temp. °C.	Scale readings.	Change for 1° C. in scale divisions.	Change for 1° C. in refractive index.
2.8	82.0	0.60	0.000360
21.8	70.5		
21.8	70.5	0.57	0.000360
38.4	61.0		

The change in scale reading for 1° C. decreases as the temperature rises and the index of refraction falls, while the change in refractive index is constant.

This is also shown in columns 7 and 8 of Table III which give the change from the first reading to the second and from the second to the third. The higher the readings, the larger is the change in scale division for 1° C.

[1] Wiley's "Principles and Practice of Agricultural Analysis," Vol. III, p. 342.

TABLE III.

	Oils.	Temperature.	First reading.	Temperature.	Second reading.	Temperature.	Third reading.	Increase 1° C.	Increase for 1° C.	Change refractive index for 1° C.	Remarks.
		1	2	3	4	5	6	7	8	9	
23605	Olive	3.4°	76.5	22.0°	65.5	37 8°	56.5	0.59	0.57	0.000366	
506	Olive	3.2°	76.0	22.2°	64.8	36.8°	56.5	0 59	0.57	0.000366	
23460	Olive	3.2°	76.0	22.2°	65.0	43.3°	53.0	0.58	0.56	0.000360	
493	Poppyseed	9.0°	82.5	19.9°	75.6	41.0°	63.2	0.63	0.59	0.000369	Gave wide blue band, making it hard to read.
491	Corn	2.8°	84.5	21.8°	73.0	39.6°	62.5	0.60	0.59	0.000366	
498	Sunflower	3.0°	81.0	21.8°	69.5	39.0°	59.5	0.61	0.58	0.000369	
23624	Sunflower	3.0°	81.2	22.0°	70.0	39.0°	60.0	0.59	0.58	0.000364	
496	Rape	2.8°	82.0	21.8°	70.5	38.4°	61.0	0.60	0.57	0.000363	
490	Rape	3.4°	82.2	22.0°	71.0	38.8°	61.4	0.60	0.57	0.000364	
486	Mustard	2.8°	84.5	22.0°	72.5	38.0°	63.2	0.62	0.58	0.000360	
495	Black mustard	3.2°	84.5	22.0°	73.0	39.4°	63.0	0.61	0.57	0.000361	
487	Lard	3.0°	74.5	22.0°	63.4	37.6°	54.6	0.58	0.56	0.000363	
22434	Lard	3.0°	75.2	22.0°	64.0	39.2°	54.0	0.59	0.57	0.000372	
499	Peanut	3.0°	78.5	22.0°	67.2	37.2°	58.5	0.59	0.57	0.000365	
23656	Peanut	3.3°	76.0	22.0°	64.5	44.2°	52.3	0.61	0.55	0.000366	
492	Peanut and cottonseed	3.4°	82.0	22.0°	70.5	42.4°	58.8	0.61	0.57	0.000369	
489	Sesame	3.4°	81.2	22.0°	70.0	38.2°	60.5	0.60	0.58	0.000370	
436	Cottonseed	3.4°	81.5	22.2°	70.0	37.6°	61.2	0.61	0.57	0.000368	
	Average									0.000365	

The oils used were partly of known purity and partly commercial oils which had been tested for adulterants. The temperatures were regulated by a current of water passing through the instrument. As there are no compensating prisms the dispersion of the oils could not be corrected and with some of the oils, especially poppy-seed which has a high dispersive power, considerable difficulty was encountered in making an accurate reading.

In fact with most of these oils there is more or less dispersion which makes an exact reading impossible, which may explain the slight differences in the change in refractive indices, rather than that there is any actual difference. As the change in refractive index for change of temperature is so much more constant than the change in scale division, it gives a much more accurate means of correcting the readings of the butyrorefractometer than can be had by use of any factor of the scale divisions.

The reading in scale division can be calculated into index of refraction, the proper correction for temperature made, and the index of refraction obtained recalculated into scale divisions. This can be readily done by means of a table prepared by Winton.[1]

For corrections for a few degrees one may use the formula

$R = R' - X(T - T')$.

R = reading corrected to T.

R' = reading at T'.

T = desired temperature.

T' = temperature at which reading was made.

X = change in scale division caused by a change of temperature of 1° C.

$X = 0.55$ for butters which read from 40° to 50° on the scale; for oils that read from 60° to 70° it equals 0.58; for oils that read from 70° to 80° it equals 0.62. Olds[2] gave the correction for temperature for olive oil and sweet almond oil, as 0.000364 for 1° C., which agrees very exactly with the results shown in Table III. Some work by J. H. Long[3] corroborates these results. He found that the correction was practically a constant for the oils he examined, but gave a little higher correction, 0.0004. H. R. Proctor,[4] in his work on the relation between the specific gravity and refrac-

[1] *Conn. Expt. Station Report* (1900), Pt. 2, p. 143.

[2] *Wied. Ann.*, **10**, 542 (1880); Landolt and Börnstein's Tables, p. 207.

[3] *Am. Chem. J.*, **10**, 392 (1889).

[4] *J. Soc. Chem. Ind.*, **17**, 1023 (1898).

tive index at different temperatures, has a large number of determinations of index of refraction at 15° C. and 60° C.

The following table of temperature corrections has been calculated by the writers from these results. Table IV shows remarkable agreement with Table III.

Oil.	Correction for 1° C. in refractive index.
Linseed	0.00037
Cotton	0.00037
Peanut	0.00037
Corn	0.00036
Sesame	0.00037
Olive	0.00037
Rape	0.00036

From these results it would seem that the correction for change in refractive index for the ordinary fats and oils is very uniform, about 0.000365 for 1° C.

THE PRODUCTION OF ACYLAMINES BY THE INTERACTION OF SODIUM SALTS OF MONOBASIC ACIDS AND AMINE HYDROCHLORIDES.

BY FREDERICK L. DUNLAP.

Received May 13, 1902.

DURING the course of some experimental work, I had occasion to try the action of sodium acetate on aniline hydrochloride. These two compounds reacted quite readily with the production of acetanilide. A brief study of this type of reaction was extended to analogously constituted bodies, the results of which experiments are given in this paper. This reaction was made use of with the sodium salts of acids containing both open and closed chains, and with alphyl- as well as with arylamines.

When the sodium salt of the monobasic aliphatic or aromatic acid is caused to react, under the influence of heat, the reaction proceeds as follows, R and R' being either an alphyl or aryl residue:

$$RCOONa + R'NH_2HCl = R'NHCOR + NaCl + H_2O.$$

In two of the experiments, conditions were varied to see the effect of temperature and mass on the yield of the resulting product, namely, in the cases where calcium and sodium acetates reacted with aniline hydrochloride. In all other cases, reaction

was brought about between molecular quantities. The calcium acetate mentioned above was the only salt other than a sodium salt made use of in this work.

No mention of such a reaction as has been outlined could be found in the literature; but after the experiments had been carried on for some time, it was found that this method had been the subject of the United States patent[1] for the manufacture of acetanilide from aniline hydrochloride and calcium or sodium acetate.

Inasmuch as this reaction took place so readily with the hydrochloride of the primary alkylamines, which we look upon as salts of substituted ammonia, there was every reason to expect that the reaction would also take place easily with ammonium chloride; and such was found to be the case, ammonium chloride reacting quite as readily as the alkylamine salts.

The reaction between the hydrochlorides of these primary alkylamines and the sodium salts of monobasic acids proceeds as follows: First, the splitting off of sodium chloride with the formation of free acid and free amine; second, the union of the amine and the acid; third, the breaking-down of the salt formed from the amine and the acid, under the influence of heat, to form the acylamine and water.

I. $RCOONa + R'NH_2HCl = NaCl + RCOOH + R'NH_2$.
II. $RCOOH + R'NH_2 = RCOONH_3R'$.
III. $RCOONH_3R' = RCONHR' + H_2O$.

In the cases where ammonium chloride was used, $R' = H$.

These stages are made sufficiently clear from the following facts: First, the formation of free acid is evidenced by the reaction resulting between sodium acetate and aniline hydrochloride, when these substances are ground together in a mortar, for a strong odor of acetic acid is developed. Then Lorin[2] has shown that when concentrated formic acid is heated in the presence of anhydrous sodium or potassium formate at 150°-155°, the formic acid decomposes into water and carbon monoxide. Formic acid alone decomposes at 160°, with the formation of hydrogen and carbon dioxide. When sodium formate and aniline hydrochloride were heated together in a sealed tube at 185°, no formamide was produced, but there was considerable gas pressure in the tube on

[1] U. S. Patents 574,395 and 574,396.
[2] *Jahresbericht*, (1876), p. 515.

opening it, due to the formic acid produced by the reaction undergoing decomposition in one, or perhaps both, of the ways indicated.

Sodium formate itself does not undergo decomposition until it reaches a much higher temperature[1]. Second, if free acid is produced by such reactions, free amine must also be produced. The production of the latter was easily distinguished in some of the experiments. The production of a free acid, say acetic, and of a free amine, for example aniline, must result in the formation of a salt—in this case aniline acetate. Third, the production of acetanilide from aniline acetate by means of heat, is a well known reaction.

As has already been stated, but two series of experiments were conducted to see the effect of temperature and mass on the yield of the resulting product. In some of the results obtained, the yield must have been very largely influenced by the fact that the mixtures were charged into the sealing tubes in a perfectly dry condition, thus precluding any very intimate contact of reacting masses. The following list shows the mixtures that were used, and the resulting products:

		Product.
1	Sodium acetate and aniline hydrochloride.....	Acetanilide
2	Calcium acetate and aniline hydrochloride.....	Acetanilide
3	Sodium acetate and *o*-toluidine hydrochloride...	*o*-Acettoluide.
4	Sodium acetate and ammonium chloride.....	Acetamide.
5	Sodium benzoate and aniline hydrochloride.....	Benzanilide.
6	Sodium benzoate and ammonium chloride.....	Benzamide.
7	Sodium benzoate and methylamine hydrochloride..	Methylbenzamide.
8	Sodium formate and aniline hydrochloride.....	.....

EXPERIMENTAL PART.

Sodium Acetate and Aniline Hydrochloride.—I. Molecular quantities of freshly fused sodium acetate and thoroughly dried aniline hydrochloride were heated, by means of an oil-bath, in a flask having a return condenser. The dry products were not intimately mixed before being introduced into the flask. Upon heating, the contents of the flask began to liquefy and turn dark. This mixture was heated for nearly three hours at 140°, and the acetanilide obtained amounted to 38 per cent. of the theoretical yield.

[1] *Ber. d. chem. Ges.*, **15**, 1507 (1882).

II. This experiment was the same as the preceding one, except that the mixture was heated for seven and a half hours on a steam-bath. Yield of acetanilide, 23 per cent. of the theory.

III. Molecular quantities of sodium acetate and aniline hydrochloride were ground together in a mortar, in order to give an intimate mixture. In a few moments after the dry salts began to be triturated, the resulting product became pasty, and finally semi-fluid. This semi-fluid mass, which smelled strongly of acetic acid, was introduced into a sealing tube, and then heated for seven hours at 120°. After this treatment, the contents of the tube were purple in color, and there was no pressure on opening the tube. Yield, 54 per cent.

IV. This experiment was carried out similarly to the preceding one, except that twice the amount of sodium acetate was employed. This mixture was heated for three hours at 165°, and a yield of 71-72 per cent. was obtained.

V. Same as No. IV, except that the temperature was held at 120° for six hours. Yield, 65 per cent.

Calcium Acetate and Aniline Hydrochloride.—I. Molecular quantities, intimately mixed in a mortar, were heated in a sealed tube for five hours at 197°. Yield of acetanilide, 58 per cent.

II. Same as preceding experiment, except that the temperature of heating was 160°, while the duration of heating was but four hours. Yield, same as in No. I.

III. Where twice the amount of aniline hydrochloride was used, *i. e.*, theoretically enough of the hydrochloride to decompose the calcium acetate, and the mixture heated in a sealed tube for seven hours at 150°, the yield of acetanilide was nearly 50 per cent.

Sodium Acetate and o-Toluidine Hydrochloride.—Molecular quantities of these compounds were ground together in a mortar to mix them intimately. On grinding, this mass acted similarly to the sodium acetate and aniline hydrochloride mixture, *i. e.*, became at first moist and pasty, and finally semi-fluid. This mass was then charged into a sealing tube and heated for eight hours at 320°. There was no pressure on opening the tube. The tube was filled with a crystalline product which was purified by crystallization from benzene. The pure product melted at 109°. Alt[1] gives the melting-point of *o*-acettoluide as 110°, and

[1] *Ann. Chem.* (Liebig), **252**, 319 (1889).

Wroblewsky[1] as 107°. From its physical and chemical properties, this body was easily recognized as *o*-acettoluide. Due to loss of mother-liquors, no yield was calculated.

Sodium Acetate and Ammonium Chloride.—Molecular quantities of these compounds were ground together as in the previous cases mentioned. During this process of grinding, the production of free ammonia was readily detected by its odor. This mixture was heated in a sealed tube for five hours at 240°. There was no pressure on opening the tube. The contents of the tube were partly liquid and partly solid; it was washed out with alcohol, the insoluble portion filtered off, and the alcoholic solution fractioned. A yield of about 40 per cent. of acetamide was obtained.

Sodium Benzoate and Aniline Hydrochloride.—Molecular quantities of these substances were intimately mixed in the usual manner. During the mixing the mass became damp, and the odor of free aniline was strongly developed. After heating in a sealed tube for four hours at 245°, the product was dark-colored, and the tube contained a crystalline product. After washing out the contents of the tube with cold water, then treating with dilute hydrochloric acid, the residue was treated with bone-black in an alcoholic solution and allowed to crystallize. When pure, the product melted at 160°; it was easily identified as benzanilide. Yield, 30 per cent.

Sodium Benzoate and Ammonium Chloride.—Molecular quantities, after mixing, were heated for eight hours at 260°. The contents of the tube were washed thoroughly with small quantities of cold water, then recrystallized from boiling water. This product by repeated crystallization could not have its melting-point raised beyond 125°. The melting-point of benzamide is usually given as 128°; for example, it is so given in Gattermann's "Praxis des organischen Chemikers". A sample of Kahlbaum's benzamide melted at 125°, and repeated crystallization would not raise it higher.

Apropos of the question of the discrepancy in the melting-point of benzamide, it is of interest to note the effect on the melting-point by the use of the two types of melting-point apparatus usually employed in these determinations. These two types, which are fully described in Gattermann's "Praxis des organischen Chemikers," differ essentially in the fact that the first has a greater

[1] *Ann Chem.* (Liebig), **168**, 162 (1873).

or less portion of the thermometer enclosed by a glass tube, the liquid in which the thermometer bulb is placed being heated with a free flame. In the second type, moreover, the thermometer stem is exposed directly to the air, the small beaker in which the bulb is placed being separated from the flame by wire gauze. In the first type heat is conveyed through the liquid by the convection currents; in the second, convection currents are done away with, as far as possible, by constant agitation with a hand stirrer.

In the first type mentioned (a 250° milk glass thermometer being used) benzamide melts from three-quarters to one degree higher than when the determination is made with the second type. The higher the melting-point, the greater will be the discrepancy in the readings between these two types. The higher reading in the first method is easily accounted for by the fact that the temperature of the air between the glass envelope and the thermometer is at a higher temperature than the air surrounding the thermometer stem in the second type. This must result in a higher reading, and one that is therefore nearer to the corrected melting-point. The melting-points given in this paper were made according to the second method.

Sodium Benzoate and Methylamine Hydrochloride.—When molecular quantities of these substances were ground together, the odor of methylamine was developed. The mixture was heated in a sealed tube for twelve hours at 280°, and on opening the tube, while there was no pressure, there was a slight odor of methylamine. The tube was filled with a pale yellow viscous liquid and some crystals. On shaking up the contents of the tube with cold water, this yellow liquid solidified. It was filtered, dried, dissolved in ether, and precipitated out with low boiling ligroïn. This method of purification is much preferable to the one given by van Romburgh,[1] who purified methylbenzamide by crystallizing from hot water. The yield of methylbenzamide obtained was 32 per cent. of the theory and it had a melting-point of 78°.

Sodium Formate and Aniline Hydrochloride.—When these compounds, intimately mixed, were heated in a sealed tube to 185° for seven hours and then cooled, the tube, on opening, exhibited considerable gas pressure and was filled with a dark liquid (aniline). From the contents of the tube no formamide was obtained.

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[1] *Rec. trav. chim. Pays-Bas*, **4**, 388 (1885).

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON.]

AN INVESTIGATION OF WOOD TAR FROM THE DOUGLAS FIR, "PSEUDOTSUGA TAXIFOLIA."[1]

BY H. G. BYERS AND PAUL HOPKINS.

Received May 17, 1902.

THE Douglas fir, better known as Oregon Pine, grows only upon the humid western slopes of the Cascade range. Its great size and its value as a source of timber makes it an important part of the natural wealth of the northwest. A number of attempts have been made to make use of the waste products in the mills of this state but without very marked success. The quantity of material destroyed by our mills is enormous. There are mills on Puget Sound which have been burning their waste for thirty years and during all that time the fires have not been out.

In view of these facts and because of almost numberless requests for information concerning the products of distillation of fir wood we decided to make some little investigation upon that subject in order to get data that would afford a comparison between our wood and that used in distillation processes in other places.

The Rainier Tar Company, of Seattle, kindly placed at our disposal a large steel retort capable of holding about three-fifths of a cord of wood. In this retort two carefully regulated runs were made. The products of the distillation were condensed in a 4-inch copper worm 125 feet in length, surrounded by cold water. All the products were carefully measured except the gas, which was estimated by difference.

The material used in the distillation was partially seasoned fir wood taken from the "butt cuts" of trees. It was cut into 2-foot lengths, weighed, and placed in the retort, which was held at as constant a temperature as possible. Not having a pyrometer at our disposal we arrived at an approximation of the temperature by means of small bars of metals placed within the retort so that the maximum temperature could be determined. In the case denominated "low run" in the following discussion at no time did the temperature rise above 420° C., the melting-point of zinc, while in

[1] *Pseudosuga mucronata* (Sargent's *silva*).

the "high run" the temperature never exceeded 700°, the melting-point of aluminum.

The time required to complete the distillation of a charge was about twelve hours, and the quantity used was about half a cord and weighed 2,500 pounds.

The results of these distillations are as follows:

	High run.	Low run.
Pyroligneous acid	34.0	47.5
Tar	17.7	7.5
Charcoal	29.0	30.0
Gas	19.3	15.0
Total	100.0	100.0

The high percentage of tar in the high run was due to the fact that it contained an abnormal quantity of water which in the course of several weeks settled out gradually. Referring the weight of water-free tar to the wood we have 6.37 per cent. for the high run and 6.00 for the low run.

PYROLIGNEOUS ACID.

The pyroligneous acid produced in the distillation was of a rich red color, that from the low run being slightly the darker. The specific gravity of the low run was 1.025; that of the high run was 1.020. The methyl alcohol was determined by conversion into methyl iodide by means of phosphorus tri-iodide. The percentages were: for the high run 2.95; for the low run 4.16 per cent. (volume). The percentage of acetic acid was determined by direct titration and found to be 2.90 per cent. for the high run and 3.47 for the low run.

TAR.

The tar was fractionated and the oil which distilled below 150°, the light oil, was investigated a little more fully than the other portions. A discussion of its constituents will be found at the close of this article. The creosote oil boiling between 150° and 250° was separated and the residue weighed as pitch.

The results of this separation are as follows:

	High run.	Low run.
Specific gravity	1.060	1.075
Watery distillate (pyroligneous acid)	64.0	20.0
Light oil	8.0	18.0
Creosote oil	10.0	23.0
Pitch	18.0	39.0

Because of the great amount of water in the one sample a more accurate comparison of the composition may be gained by referring these values to water-free tar as:

	High run.	Low run.
Light oil	22.2	22.5
Creosote oil	27.8	28.7
Pitch	50.0	48.8

The creosote in the creosote oil was separated in the usual way and found to be 17 per cent. of the oil or 5 per cent. of the tar. The percentage of guaiacol in the creosote was also determined and found to be about 9.5 per cent.; the method used was that given in Allen's "Commercial Organic Analysis," Vol. II, Part II, p. 284. The creosote is almost colorless, has a smoky aromatic odor and a specific gravity of 1.065. It seems almost identical with the product of beech-wood tar. The pitch from the tar is black or very dark brown and resembles closely in appearance coal-tar pitch but has not the same odor or taste.

Since great quantities of Stockholm tar are imported for the local market and it commands a high price, it seemed worth while to compare our product with that and also with pine tar. We found that by removing the water and a certain amount of the light oil, a tar could be obtained which resembles Stockholm tar very closely. The color suffers somewhat in the redistillation yet the tar as obtained can not be otherwise distinguished from Stockholm tar, even by the tests usually given for identification of the latter.[1] A fair idea of the variations may be gained from the following table:

	Fir tar.	Stockholm tar.	Pine tar.
Color	Black (almost).	Brownish black.	Brown.
Odor	Smoky but characteristic.	Smoky.	Resinous.
Consistency	Sirupy.	Sirupy.	Viscid.
Specific gravity	1.100	1.090	1.110
	Per cent.	Per cent.	Per cent.
Light oil	3	3	5
Creosote oil	34	30	40
Pyroligneous acid	4	5	2
Pitch	59	62	53
Hardness of pitch	Brittle.	Less brittle.	Soft.
Color of pitch	Black.	Black.	Brown.

[1] Allen's "Commercial Organic Analysis."

The light oil which is separated from the tar by this redistillation has a specific gravity of 0.945 and when freshly distilled is of a clear amber color but darkens markedly on standing.

THE CHARCOAL.

There was no attempt made to distinguish between the samples of charcoal made at the different temperatures. The quantities were nearly the same and they were similar in appearance. The coal is soft and retains the porous structure of the wood. It is, however, remarkably free from ash.

THE GAS.

No attempt was made to analyze the gas given off in this distillation and its amount was determined by difference. This gas is, however, utilized in the processes of the refining of the wood products. It is non-illuminating and hence cannot be used directly as an illuminant, except in Welsbach burners, in which it gives an excellent light. A series of tests was made on this subject in the city of Tacoma and a sample of the gas was sent us for analysis. The temperature at which it was produced was much higher than those of our experiments and the retort was arranged to decompose almost totally all the tar produced. The results are as follows:

	Per cent.
Light hydrocarbons	6.3
Heavy hydrocarbons	0.0
Methane	7.3
Carbon monoxide	28.8
Hydrogen	30.6
Carbon dioxide	12.3
Nitrogen	14.7

THE LIGHT OIL.

In addition to the foregoing experiments we decided to compare our light oil with that obtained from hard woods as given in an investigation by G. S. Fraps.[1]

This was not fully carried out by reason of lack of time but a few points of interest were developed. Only that portion of the oil boiling below 140° was used. Fifteen liters of the light oil were first fractioned into six fractions—below 75°; 75°-90°; 90°-105°; 105°-120°; 120°-135°; 135°-150°. These portions were then

[1] *Am. Chem. J.*, **25**, 26.

fractioned, through a Hempel tube, five times and the fractions collected for every five degrees.

It was found that a small portion passed over before 50° was reached and indeed a little before 40° but this is included in the portion 40°-50°. The following table shows the result of this fractionation in percentage of total oil:

Fraction.	Per cent.	Fraction.	Per cent.
40°– 50°	0.37	105°–110°	0.87
50°– 55°	0.47	110°–115°	0.43
55°– 60°	0.77	115°–120°	0.53
60°– 65°	0.55	120°–125°	0.40
65°– 70°	0.62	125°–130°	0.37
70°– 75°	0.70	130°–135°	0.002
75°– 80°	0.57	135°–140°	0.73
80°– 85°	0.93	40°–140°	13.68
85°– 90°	0.94		
90°– 95°	1.40		
95°–100°	1.37		
100°–105°	0.97		

The table shows five points of accumulations of distillate but they are not so marked nor is the percentage of oil coming over below 140° nearly so great as in the oil investigated by Mr. Fraps. The color of the oily distillates varied from colorless to almost black and always darkened upon standing, but the change was not regular.

SOLUBILITY.

The solubility of the fractions was determined by shaking 2 cc. of the oil in a graduated pipette with 10 cc. of water, and determining the loss of volume. The results follow:

Fraction.	Solubility. Per cent.	Fraction.	Solubility. Per cent.
40°–50°	55	85°–90°	30
50°–55°	52	90°–95°	27
55°–60°	50	100°–105°	20
60°–65°	44	105°–110°	16
65°–70°	40	110°–115°	12
70°–75°	35	115°–120°	12
75°–80°	34	120°–125°	10
80°–85°	32	125°–130°	10
		130°–135°	9
		135°–140°	9

It will be noticed that the solubility of this oil is greater for corresponding fractions than in the hard wood oil.

KETONES AND ALDEHYDES.

The ketones and aldehydes were removed from each fraction by shaking with a concentrated solution of acid sodium sulphite, keeping the mixture cool during the reaction. The crystalline precipitates were filtered by suction through muslin, and dried. A second precipitation with sulphite was always attempted. As in the hard oil, the precipitates from the lower fractions were distinctly crystalline and became more gelatinous with the higher fractions, but, curiously, when the higher fractions were reached, *viz.*, from 100° upward, the precipitates became crystalline again. In filtering the lower fractions a strong odor as of acrolein was developed.

The precipitates contained very small quantities of aldehydes. Assuming that half the weight of the dried precipitate is the volume of the ketone the following approximation is reached.

Fraction.	Ketones. Per cent.	Fraction.	Ketones. Per cent.
40°–50°	2.2	95°–100°	1.1
50°–55°	5.7	100°–105°	1.1
55°–60°	9.7	105°–110°	1.0
60°–65°	6.3	110°–115°	2.5
65°–70°	2.2	115°–120°	2.2
70°–75°	3.9	120°–125°	1.7
75°–80°	2.2	125°–130°	1.4
80°–85°	2.1	130°–135°	1.0
85°–90°	4.3	135°–140°	4.4
90°–95°	1.6		

It will be seen that while there is not nearly so large a percentage of ketones in the fir as in the hard oil yet there are marked accumulations at 55°-60° (this is probably acetone), at 70°-75°, at 85°-90°, and at 135°-140°. We attempted to separate the ketones from the sulphite fractions, but the quantities were too small to be of use in further investigation. However, in the fraction 125°-130° a test was made for mesityl oxide which was not found by Mr. Fraps in the hard oil. The solution was distilled with strong caustic soda and a strong odor of peppermint was developed, showing the possible presence of mesityl oxide.

ETHEREAL SALTS.

The residual oil after removal of the ketones was dried and fractionated. The fractions were shaken with a caustic soda solution (1:4) for fifteen to twenty hours. To accomplish this the

glass-stoppered bottles were fastened to the face of a wooden pulley about 8 inches in diameter which made nine revolutions per minute. The oils were measured before and after saponification and the loss in volume was considered to be due to the saponification of ethereal salts. This loss was for each fraction as follows:

Fraction.	Per cent.	Fraction.	Per cent.
40°–50°	20	90°–95°	18
50°–55°	23.5	95°–100°	20
55°–60°	27	100°–105°	19
60°–65°	24	105°–110°	13.9
65°–70°	25	110°–115°	17.6
70°–75°	25	115°–120°	15.6
75°–80°	18.5	120°–125°	20.7
80°–85°	31	125°–130°	38.5
85°–90°	15.5	130°–135°	25.4
		135°–140°	27.1

It will be observed that there are marked accumulations at certain temperatures and also that there is no marked decrease in the amount of oil saponified as the boiling-point of the fraction rises. In the higher boiling fractions a gummy solid of a yellow color was formed, which while insoluble in water dissolved easily to a purple solution in nitric, hydrochloric, or sulphuric acids. This color was not destroyed by boiling but disappeared on standing and on addition of water. No attempt to discover its nature was made.

The caustic soda solutions of the ethereal salts were distilled to remove alcohols. No odor of ammonia was developed.

The alcoholic distillates were all found to contain methyl alcohol by the test of Mulliken and Scudder.[1] The alcoholic distillates were also treated with iodine and caustic potash and always gave a decided test for ethyl alcohol.

The acids were now freed by addition of sulphuric acid and distilled.

The silver salts precipitated from the fraction boiling at 40°-50° gave 68.74 per cent. silver. Calculated percentage of silver in silver formate is 70.59; in silver acetate 64.66. The acid was therefore probably a mixture of the two, since methyl formate boils at 30.4° and some of the oil passed over before that temperature was reached. The silver salt of the 50°-55° fraction gave:

[1] *Am. Chem. J.*, **24**, 444.

	Found.	Formic acid.	Acetic acid.
Percentage of silver	65.44	70.59	64.66

This result we take to indicate the presence of ethyl formate (54.9°) and methyl acetate (57.3°).

The silver salt from fraction 55°-60° gave 64.99 per cent. of silver (calculated for acetic acid, 64.66). It hence consisted almost entirely of methyl acetate (57.3°).

The presence of acetic acid was also indicated by qualitative tests in fraction 70°-75°. Satisfactory results from the silver salt were not obtained because of the small quantity at our disposal.

The same statements apply to fractions 75°-80° in which the boiling-point and odor indicate the presence of methyl propionate (79.5°).

From the fraction 102°-105°, by acidifying with sulphuric acid, an oil separated which was by odor butyric acid and indicates the presence of methyl butyrate (102.3°).

The investigation was necessarily interrupted at this point but will probably be taken up at some future date.

There seems to be enough of interest in the wide difference between this oil and that from other varieties of wood to warrant further investigation.

SEATTLE, WASH.,
March 3, 1902.

INVESTIGATION OF THE OIL OF THE RED ELDERBERRY, "SAMBUCUS RACEMOSA ARBORESCENS."

BY H. G. BYERS AND PAUL HOPKINS.

Received May 17, 1902.

ON the western slopes of the Cascade Mountains and on the lowlands about Puget Sound grow great quantities of a red elderberry which, by reason of its large size, is denominated a variety of the species *racemosa*. The berries are a bright crimson and serve as food for birds but because of an unpleasant odor and the presence in them of a considerable quantity of a yellow oil are not used by the people as food nor are they converted into wine.

An investigation of this oil was made with the following results. From about 10 gallons of the berries it was possible to get about 500 cc. of the oil by pressing the juice from berries and ex-

tracting with ether the layer of crude oil which rose to the surface of the liquid. The oil as obtained from the ether solution by spontaneous evaporation is of a light yellow color but darkens markedly on standing or when the ether is evaporated by means of a water-bath.

The oil has a specific gravity of 0.9072 at a temperature of 15° C. It solidifies at —8° and melts at about 0°. It has no definite boiling-point but decomposes when distilled even at a pressure of 20 mm. It proved to be a mixture of the glycerides of the fatty acids and contains 6.65 per cent. free acid calculated as oleic acid. Because of a marked resemblance to olive oil a very careful determination of its constants and composition was made.

Unsaponifiable Matter.—The unsaponifiable matter of the oil, which contained the characteristic odor of the oil, formed 0.66 per cent. of the whole. It crystallizes in light yellow hexagonal plates.

Glycerol.—The fats were saponified and the glycerol determined, the amount being 11.4 per cent.

Fatty Acids.—The lead salts of the acids were made and thoroughly extracted with ether in a Soxhlet apparatus. The insoluble residue was converted into its barium salt and crystallized from alcohol in three fractions. These fractions gave the following results when their barium content was determined as barium sulphate.

	I.	II.	III.	Calculated for palmitic acid, $C_{16}H_{32}O_2$.
Percentage of barium	21.06	21.24	20.14	21.17
	21.11	21.21	20.13	....

The crystals from the first two fractions were white plates. The third fraction was discolored by the impurities of the mother-liquor. The oil evidently contains no saturated fatty acid save palmitic acid.

The solution of the lead salts in ether was fractionally crystallized and converted into the barium salt. The barium salt was refractionated and the barium determined in the first fraction.

		Calculated for oleic acid, $C_{18}H_{32}O_2$.
Percentage of barium.....	19.46	19.59
	19.38	....

The iodine absorption of the fatty acid from this fraction was also 90.6 and 89.5, the calculated value for oleic acid being 90.07.

A number of fractional precipitations of the potassium salt of the mixed acids were made from a weakly ammoniacal solution by means of barium chloride.

The iodine numbers of the free acids from these fractions were:

Fraction.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Iodine number.	21.0	36.2	88.2	89.3	87.3	90.6	111.3	120.6
Quantity of salt	2.0	1.2	1.5	1.0	1.0	0.8	0.5	2.0

The fatty acid from VII and VIII was highly colored and somewhat impure from oxidation, yet the results indicate the presence of an acid, probably linoleic, having an iodine absorption greater than that of oleic acid. If linoleic acid, it is present to an extent of not less than 7-8 per cent.

The presence of soluble acids was determined by the method of Muter.[1] The Reichert-Meissl number being but 1.54, thus showing the practical absence of butyric or other volatile acid, the results of the titrations were calculated to an acid having a molecular weight of 136, which is the mean of the molecular weights of capric, caprylic, and caproic acids. The results showed the presence of 2.95 per cent. of these acids.

The quantity of palmitic and oleic acids was determined by Lang's "Modification of Muter's Method".[2] The results show oleic acid and linoleic acid 72 per cent.; palmitic acid 21.66 per cent. The saponification equivalent was found to be 209.3.

The Hehner number is 91.75.

From the results indicated in the foregoing discussion the properties and composition of the oil are as given below. For convenience of comparison the corresponding values for olive oil are given in parallel.

	Elderberry oil. Per cent.		Olive oil. Per cent.	
Palmitin	22.0		28.0	
Olein and linolein	73.6	92.2 7.8	72.0	93 7
Caprin, caproin and caprylin	3.0		....	
Unsaponifiable matter	0.66		....	

[1] Allen's "Commercial Organic Analysis," Vol. II, Part I, p. 189.
[2] *Pharm. J.*, **59**, 61.

	Elderberry oil.	Olive oil.
Specific gravity	0.907	0.914–0.917[1]
Solidifying point	—8°	2°
Melting-point of fatty acids	38°	26°
Saponification equivalent	209.3	191.7
Iodine number	81.44	80–82
Hehner number	91.75	94.03
Reichert-Meissl number	1.54	1.50
	Per cent.	Per cent.
Free acid	6.65	8.07

SEATTLE, March 14, 1902.

A VOLUMETRIC METHOD FOR THE ESTIMATION OF SULPHURIC ACID IN SOLUBLE SULPHATES.

BY YASUJURO NIKAIDO.

Received September 12, 1901.

THE method is based on the following reactions:

(1) $K_2SO_4 + Pb(NO_3)_2 = PbSO_4 + 2KNO_3$.

(2) $2KI + Pb(NO_3)_2 = PbI_2 + 2KNO_3$.

Under proper conditions it was found that lead salts will not react with iodides in the presence of sulphates until all the sulphuric acid has been precipitated by the lead, whereupon the yellow color of the lead iodide becomes visible. It is, therefore, possible to use potassium iodide as an indicator for the end reaction between lead and sulphuric acid.

To test the accuracy of the method, N/10 solutions of lead nitrate and of potassium sulphate were used. Then 10 cc. of the potassium sulphate solution were taken, about 0.2 gram of potassium iodide added and the solution was titrated with a lead nitrate solution. It was found that on adding lead nitrate, lead iodide was first formed, imparting a yellow color to the solution. This color quickly disappears, owing to the formation of lead sulphate. As soon as all the sulphuric acid is precipitated the yellow color becomes permanent. In water solutions alone, however, the reaction is not complete, lead sulphate being somewhat soluble in water and the yellow color of the lead iodide showing slightly, even when an excess of potassium sulphate is present.

To avoid this, it was determined to try the reaction in an alco-

[1] Meyer and Jacobson: "Lehrbuch," Vol. I, p. 594.

holic solution, and for this purpose another 10 cc. of the potassium sulphate solution were taken together with about 0.2 gram of potassium iodide. Alcohol was then added until a slight precipitate of potassium sulphate was formed, and then the lead nitrate solution was carefully added. It was found that the color of lead iodide appeared just about when 10 cc. of lead nitrate solution had been added.

Experiments were made to find out in what strength of alcohol the reaction best takes place. Since in water alone it is impossible to obtain any satisfactory results, 25 per cent. alcohol was first used. With this, it was also impossible to obtain good results. Then a titration was made using 35 per cent. alcohol, but still the results were not satisfactory. In 40 per cent. alcohol the results were fair, but the reaction took place very slowly. In 50 per cent. alcohol, the results were fairly satisfactory, although the reaction was still slow. The results obtained from the titrations in 60 per cent. alcohol were satisfactory, and the reaction was moderately rapid. The titrations in 65 per cent. alcohol gave very satisfactory results, and the reaction went quite rapidly with the following results:

N/10 potassium sulphate solution. cc.	N/10 lead nitrate. solution. cc.
5.00	5.02
10.00	10.05
11.25	11.22
19.97	20.01
Average 1.00	1.0017

The results from the titrations in 70 per cent. alcohol were obtained in the same manner as in the 65 per cent. alcohol. It was found at this point, *viz.*, with 70 per cent. alcohol, or over, the reaction began to go more slowly and to become increasingly difficult to complete, owing to the insolubility of potassium sulphate in alcohol. The experiments show therefore that the reaction goes best in alcoholic solutions from 50 to 70 per cent.

Experiments were made to find out what effect various acids have upon the reaction. It was found that no satisfactory results could be obtained in the presence of free nitric acid, since it liberates iodine from potassium iodide and makes it difficult to see the color of the end reaction. In the presence of hydrochloric acid,

the reaction does not take place normally, because lead iodide is converted into a pale yellow compound (probably a double halogen salt of lead) which is not decomposed by neutral sulphates. The same compound is formed when a large quantity of chlorides is present. Small quantities of chlorides do not affect the titration. In the presence of free acetic acid the reaction takes place regularly and satisfactorily, but sodium acetate interferes with the titration, owing to the very considerable solubility of lead iodide in sodium acetate. The titrations were made also in the presence of free oxalic and tartaric acids. In the oxalic acid solution lead was precipitated, but not in the tartaric acid solution. In presence of potassium tartrate, lead was precipitated.

To determine the applicability of this method to stronger solutions of sulphates, a N/2 solution (43.47 grams per liter) of potassium sulphate was used. Portions of this solution were titrated with an N/2 solution (82.5425 grams per liter) of lead nitrate. It was found that in this case the titration was most satisfactory, using 50 per cent. to 60 per cent. alcohol.

The results were as follows:

N/2 potassium sulphate solution. cc.	N/2 lead nitrate solution. cc.
10.82	10.87
20.07	20.10
30.22	30.20
40.35	40.30
Average 1.00	1.00

Having in the manner indicated determined the accuracy of the method under the conditions mentioned, its applicability for the estimation of sulphuric acid in other sulphates was next tried. The substances used were magnesium sulphate, zinc sulphate, ferrous ammonium sulphate, copper sulphate, manganous sulphate, ferrous sulphate, and ferric ammonium sulphate.

In the titration with ferrous ammonium sulphate a few drops of acetic acid were added to prevent the formation of insoluble basic compounds. In the case of copper sulphate the copper was precipitated with zinc or aluminum and the titration carried out as usual after acidifying the solution with acetic acid in order to prevent the formation of precipitates of basic sulphates.

In the case of ferric ammonium sulphate, the iron was precipi-

tated with potassium hydroxide. The solution and precipitate were then transferred to a graduated flask and made up to a definite volume. The precipitate was allowed to settle and an aliquot part of the supernatant solution was taken and acidified with nitric acid, evaporated to dryness to expel free nitric acid, dissolved in water, alcohol added, and the solution titrated with lead nitrate. The error due to the volume of the ferric hydroxide is negligible in an N/10 solution in comparison with the errors of titration. In these determinations, pure substances which were obtained by recrystallization, and with each, semi-normal solutions were used. The results in all these titrations were fair and satisfactory.

The following precautions should be carefully observed. The titrations should never be made in warm solutions as lead iodide is soluble in hot water. The titrations should not be made in a large volume of solution as lead iodide is slightly soluble even in cold water.

It is probable that the method is applicable to all soluble sulphates, provided:

(1) That the operation is carried out in dilute alcohol, that is, 50-70 per cent. alcohol in case a tenth-normal solution of lead nitrate is used, and 50-60 per cent. alcohol in case a semi-normal solution of lead nitrate is used.

(2) That nitric acid, hydrochloric acid, sodium acetate and substances that will form insoluble compounds with lead are avoided.

(3) That in the case of colored sulphates, the base which gives color to the compound is removed by precipitation, *e. g.*, in the case of copper sulphate, the copper is precipitated, using zinc or aluminum; in the case of ferric ammonium sulphate, the iron is precipitated with potassium hydroxide.

(4) That in the case of the sulphates of the heavy metals, such as ferrous sulphate, ferrous ammonium sulphate, zinc sulphate, etc., a few drops of acetic acid are added to prevent the formation of basic sulphates.

(5) That the titrations are made in small volumes of cold solution, using about 0.2 gram of the potassium iodide to each 25 cc. of the solution.

Finally, it may be claimed for the method here proposed, that its

accuracy, rapidity, ease of manipulation and general applicability should render it more satisfactory than any of the previously known volumetric methods for the estimation of sulphuric acid.

The method may also be used for the estimation of lead in soluble compounds of lead by reversing the operation.

A PRELIMINARY NOTE ON THE OIL OF MILFOIL.

BY A. B. AUBERT.

Received April 30, 1902.

THE specimen examined was distilled by Metzner and Otto, of Leipzig. It is of a dark bluish green color and has a mild and pleasant odor. Specific gravity at 22° equals 0.9217. Refractive index, 1.506 at 20°. It is soluble in absolute alcohol, ether, xylene and chloroform; also in about 6.5 volumes of 95 per cent. alcohol with a slight residue of brownish colored oil.

It was distilled under reduced pressure with the following results:

One hundred volumes of the oil yielded:

7 parts by volume between 170°-190°.
17 parts by volume between 190°-210° (sp. gr. 0.900).
50 parts by volume between 210°-220° (sp. gr. 0.907).
9 parts by volume between 220°-235° (sp. gr. 0.936).
3 parts by volume above 235°.

The residue, constituting 14 parts, remaining in the flask was a semi-solid, dark olive-brown, waxy substance, hardly soluble in cold alcohol, partly soluble in boiling alcohol, yielding a dark yellow-brown solution. The insoluble residue was of a greenish brown color, somewhat resembling paraffin in consistency. By evaporation of the alcoholic solution a dark yellow-brown pitch was obtained.

The oil has a slightly acid reaction.

The products of distillation gave the following reactions:

170°-190°, slightly acid.
190°-210°, nearly neutral.
210°-220°, nearly neutral.
220°-235°, slightly acid.

(This distillate contained products of decomposition.)

That portion distilling between 170°-190° was tested for cineol,

with no very satisfactory results, the conclusion being that but a small amount of cineol is present.

The oil was examined for aldehydic constituents with sodium bisulphite. A slight precipitate formed which, upon decomposition with caustic potash, yielded traces of a substance having a faint odor somewhat similar to that of cedar wood.

A test was made for acids, but the quantity present was too small to give any definite results.

No sulphur compounds were detected. All the distillates exhibited traces of blue color. That portion distilling between 210° and 220° had a color very similar to that of a solution of copper sulphate, while that coming over at 220°-235° was much deeper in color but of a greenish blue shade.

The blue distillate (210°-220°) was redistilled, the greater part passing over at 214°. This was put away in a tightly corked bottle and after about a year and a half was examined. During that time its color had become quite light and changed to a yellowish green, though it had been carefully kept in darkness.

The ultimate analysis gave the following results:

	Oil. Gram.	C. Gram.	H. Gram.
No. I.....	0.3691	0.288	0.0400
No. II.....	0.3302	0.2886	0.0406

The molecular weight determination by the boiling-point method gave as results 164.5 and 165, which would correspond to the formula $C_{12}H_{20}$. The above determinations were performed by Mr. C. D. Holley, M.S., one of my former students.

The rotary power is —14.2° for 100 mm. tube. Refractive index, 1.492. It boils at about 254° (uncorr.) at 754.8 mm. pressure, undergoing slight decomposition. This substance exhibits most of the reaction of the terpenes.

A small quantity (5 cc.) was diluted with alcohol and ether (20 cc. each), kept cool, and bromine slowly added. The action was quite energetic, the light yellowish green solution soon changing to very dark green.

The alcohol and ether were driven off in a warm closet, leaving a greenish black pitchy residue which continued to emit hydrobromic acid for a long time. Ten cc. were diluted with 30 cc. of benzene, kept cool, and a steady current of dry hydrochloric acid gas passed through for an hour and a half. It was, at

first, quite rapidly absorbed, the liquid becoming red-purple and finally purplish brown. Upon evaporation of the benzene a dark brown, viscid liquid remained. A few drops were placed upon a watch-glass and several scales of iodine added For a moment no action was noticed. Very soon however a violent reaction set in, considerable of the iodine being vaporized thereby. The result of the reaction was a dark, sticky, resinous mass.

The remaining quantity of the distillate was so small that further tests had to be suspended. But from the examination made it would seem that the blue distillate obtained from this specimen of the oil of milfoil is not identical with that from the oil of chamonile. It is evidently closely related to the terpenes.

The quantities of the other distillates were too small for extended examination.

UNIVERSITY OF MAINE,
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NEW BOOKS.

THERMODYNAMIQUE ET CHEMIE. By P. DUHEM. 16 x 25 cm. pp. ix + 496. Paris: A. Hermann. 1902.

This is primarily a book on the phase rule, written for the chemist and not for the mathematical physicist. The first chapter deals with work and kinetic energy, the second with heat and internal energy. These two chapters are really introductory thermodynamics. We next have a chapter on heat effects and then one on chemical equilibrium. In the sixth chapter there is a discussion of the theorem of Carnot-Clausius, and of the thermodynamic potential. In the seventh chapter we find the phase rule outlined and ten chapters are devoted to the application to concrete cases. The general order is: multivariant systems, univariant systems, inversion points, displacement of equilibrium, systems with constant boiling- or melting-points, solid solutions, critical states, dissociation of gases. This comprehensive survey is followed by a chapter on apparent false equilibria and by one on false equilibria while the last two chapters are on systems with a non-uniform temperature and on chemical dynamics and explosions.

While one must regret that the arrangement of material is so haphazard, the way the material is treated is excellent and will

quicken interest in the subject. The treatment of indifferent points is especially complete and the reader will also get much profit from the chapters on solid solutions. The cream of the book, however, is to be found in the part on false equilibria and that in spite of one serious blemish. A number of experiments on false equilibria have been made in Duhem's laboratory or under his guidance and most interesting results have been obtained. These results have, however been called in question by Bodenstein who asserts that experimental error and a belief in the theory have led Duhem's scholars astray. This charge has never been met and there is no reference to Bodenstein in the book. This leaves matters in a most unfortunate position. The work of Pélabon, Hélier and others is very important, if correct, but not so important otherwise. As matters now stand, many chemists believe that there are reactions which do not start at a given temperature but there are very few who believe that a reaction runs part way and then stops short of a true equilibrium. Duhem's conception of "chemical friction" is a very valuable one, even though the experimental data are not above suspicion. Roloff's work on the cryohydrates appears to have been overlooked.

WILDER D. BANCROFT.

REFRIGERATION, COLD STORAGE, AND ICE-MAKING. By A. J. WALLIS-TAYLOR, C.E. London: Lockwood & Son; New York. D. Van Nostrand Co. Price, $4.50 net.

This practical treatise on the art and science of refrigeration is based on and embodies to a large extent the personal experience of the author. English methods and processes are most fully described. The whole subject is handled in a capable manner and the treatise will be found of service to teacher and student, and mainly to the technical engineer and those actually engaged in the various industries using refrigeration. The chemistry of refrigeration is only very superficially mentioned.

In an interesting table of the principal freezing mixtures, the author gives the reduction of temperature for a mixture of snow 3 to potassium 4 (?) as the maximum, 32° F. to —51° F. The lowest temperature obtainable by such mixtures is for snow 8 to dilute sulphuric acid 10 from —68° to —91° F., the materials themselves having been previously cooled. The subject-matter is classified under five principal heads:

I. The chemical processes, wherein the more or less rapid dissolution or liquefaction of solids is used to abstract heat.

II. The vacuum systems, wherein the abstraction of heat is produced by a partial evaporation of the substance, with the use of mechanical devices, such as pumps, etc.

III. The compression processes, wherein the abstraction of heat is effected by mechanical compression and the cooling of a separate agent, more or less volatile.

IV. The absorption system, wherein the abstraction is indirect, effected by direct heat on a separate agent, more or less volatile, which enters into solution with a liquid.

V. The cold air methods, wherein air or gases are compressed and cooled, and expansion takes place while doing work, an application of heat to ultimately produce cold.

The first ten chapters of the treatise, some 200 pages, are devoted to the description of these processes, and the other eleven chapters, 300 pages, being taken up with the application of these processes to refrigeration, classed under the following chapters: Cocks, Valves, Pipe-Joints and Unions; Refrigeration and Cold Storage; Marine Refrigeration; Ice-Making; The Management and Testing of Refrigeration Machinery; Cost of Working; Production of Very Low Temperatures. The sub-division of the chapter on Manufacturing, Industrial and Constructional Applications gives a very good idea of the whole character of this treatise; *viz.*, chocolate manufacture, breweries, paraffin works, artificial butter manufactories, dairies, dynamite factories, manufactories of photographic accessories, wine growers' and wine merchants' establishments, distilleries, sugar factories and refineries, chemical works, India rubber works, glue works, tea factories, and others, also manufacturing and industrial applications, tunnelling, sinking shafts, laying foundations, etc.

The book is profusely illustrated with some 300 wood cuts descriptive of processes and plants. The table of contents and index are complete. An appendix of useful tables and memoranda, and list of illustrations will be found of service. The book is comparatively free from errors. The use of the metric system in place of English weights and measures, and of the centigrade scale in place of the Fahrenheit, would be an improvement. The author has made free use of the literature on the subject, inclusive of

1901, relying for his American data on this completely. Full credit is given to others. The reluctance must be commended with which the author abstains from giving undue or special credit to any special process or machinery, thereby advertising same.

The treatise can be recommended as a useful and up-to-date description of the processes of refrigeration and their application to the arts.

EDWARD GUDEMAN.

MODERN CHEMISTRY, WITH ITS PRACTICAL APPLICATIONS. By FREDUS N. PETERS, A.M., Instructor in Chemistry in Central High School, Kansas City, Mo. New York: Maynard, Merrill & Co. 1901.

This text-book is intended to be used in secondary schools. As stated in the preface the author has endeavored to avoid giving too great a number of facts, to omit what can never be of interest or value to beginners and has tried to show, wherever possible, the practical applications of the science to every-day life and has emphasized industrial and commercial processes. At the same time the fundamental principles of the science have not been forgotten and due attention has been given to these.

On the whole the author has succeeded very well and this book is much superior to many that are now in use. After two introductory chapters, one on chemical and physical changes and the other on valence, which it would have been better to put later or omit altogether, he begins with water and then takes up hydrogen and oxygen. This is followed by nitrogen, the atmosphere, the halogen elements and carbon and a few of its simpler compounds. Then follows a chapter on the laws of definite and multiple proportions and combining weights. Sulphur, silicon and phosphorus are then considered after which a chapter is given up to Avogadro's law and atomic weights. Before considering the metals a very brief mention is made of the periodic law. The subjects are everywhere treated very briefly and concisely and the references to commercial processes are very elementary. The appendix contains directions for the qualitative analysis of simple substances.

There are a few errors which no doubt will be corrected in the next edition. Thus for example on page 147 the name ethane is given to olefiant gas. On page 224 plaster of Paris is referred to as anhydrous calcium sulphate. On page 226 the statement is made that the hardness of water is either "temporary or perma-

nent according as it can be removed by boiling or adding ammonia or not at all." It would have been well in this connection to have explained to the student how permanent hardness can be removed. On page 236 the explosive copper acetylide is given the formula CuC_2 instead of Cu_2C_2. The cut on page 290 should be omitted.

Taken as a whole the book is to be commended, and it will undoubtedly find an extended use in high schools and academies.

EDWARD H. KEISER.